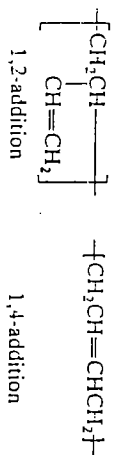


The preceding polymers would thus be named as follows:

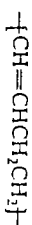
Source name	IUPAC name
Polyethylene	Poly(methylene)
Polytetrafluoroethylene	Poly(difluoromethylene)
Polystyrene	Poly(1-phenylethylene)
Poly(acrylic acid)	Poly(1-carboxyethoxyethylene)
Poly(α -methylstyrene)	Poly(1-methyl-1-phenylethylene)
Poly(1-pentene)	Poly[1-(1-propyl)ethylene]

In the IUPAC system, parentheses are always used following the prefix; also ethylene (rather than ethene) is the acceptable structural name. Furthermore, the IUPAC system makes no distinction between polyethylene and polymethylene.

Diene monomers such as 1,3-butadiene ($\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$) create special difficulties because they can undergo both 1,2- and 1,4-addition. Thus poly(1,3-butadiene) may have two possible repeating units:



with the latter capable of exhibiting *cis-trans* isomerism. To name the polymer by IUPAC rules, the CRU of the 1,4-addition product is best written in the less familiar format:



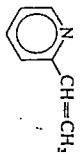
Assuming each butadiene polymer were to consist of a single repeating unit, the names would be as follows:

Source name	IUPAC name
1,2-addition	1,2-Poly(1,3-butadiene)
1,4-addition	1,4-Poly(1,3-butadiene)
	Poly(1-butene-1,4-diyl)

The prefixes *cis* and *trans* are placed in front of the name, as appropriate, for the 1,4 polymer. Until recently the IUPAC had recommended the name poly(1-butenylene) for the 1,4 polymer, but this has been changed to identify (by "1,4-diyl") the bonds linking the repeating units. The source-based names are commonly simplified to 1,2-polybutadiene and 1,4-polybutadiene.

In polydiene synthesis, both repeating units and stereochemistries are invariably present in the final product, with one predominating depending on the reaction conditions. This is explored more fully in Part II. Other aspects of polymer stereochemistry are discussed in Chapter 3. Some additional examples of vinyl polymer nomenclature are given in Table 1.2.

TABLE 1.2. Representative Nomenclature of Vinyl Polymers

Monomer Structure	Monomer Name	Polymer Repeating Unit	Source Name	IUPAC ^a Name
$\text{CH}_2\text{CH}=\text{CH}_2$	Propylene	$\left[\begin{array}{c} \text{CH}_2\text{CH} \\ \\ \text{CH}_3 \end{array} \right]$	Polypropylene	Poly(propylene)
$\text{CH}_2=\text{CHCl}$	Vinyl chloride	$\left[\begin{array}{c} \text{CH}_2\text{CH} \\ \\ \text{Cl} \end{array} \right]$	Poly(vinyl chloride)	Poly(1-chloroethylene)
$\text{CH}_2=\text{C}(\text{CH}_3)_2$	Isobutylene	$\left[\begin{array}{c} \text{CH}_2\text{C} \\ \\ \text{CH}_3 \end{array} \right]$	Polyisobutylene	Poly(1,1-dimethylethylene)
$\text{CH}_2=\text{CHCN}$	Acrylonitrile	$\left[\begin{array}{c} \text{CH}_2\text{CH} \\ \\ \text{CN} \end{array} \right]$	Polyacrylonitrile	Poly(1-cyanoethylene)
$\text{CH}_2=\text{CCO}_2\text{CH}_3$	Methyl methacrylate	$\left[\begin{array}{c} \text{CH}_2\text{C} \\ \\ \text{CH}_3 \\ \\ \text{CO}_2\text{CH}_3 \end{array} \right]$	Poly(methyl methacrylate)	Poly(1-(methoxycarbonyl)-1-methylethylene)
$\text{CH}_2=\text{CHOCCH}_3$	Vinyl acetate	$\left[\begin{array}{c} \text{CH}_2\text{CH} \\ \\ \text{OCCH}_3 \end{array} \right]$	Poly(vinyl acetate)	Poly(1-acetoxyethylene)
	2-Vinylpyridine	$\left[\begin{array}{c} \text{CH}_2\text{CH} \\ \\ \text{N} \end{array} \right]$	Poly(2-vinylpyridine)	Poly(1-(2-pyridinyl)ethylene)
$\text{CH}_2=\text{C}(\text{CH}_3)-\text{CH}=\text{CH}_2$	Isoprene	$\left[\begin{array}{c} \text{CH}_2\text{C} \\ \\ \text{CH}_3 \\ \\ \text{C}=\text{CH}_2 \\ \\ \text{H} \end{array} \right]$	<i>cis</i> -1,4-Polyisoprene	<i>cis</i> -Poly(1-methyl-1-butene-1,4-diyl)
$\text{CH}_2=\text{C}(\text{Cl})-\text{CH}=\text{CH}_2$	Chloroprene	$\left[\begin{array}{c} \text{CH}_2\text{CH} \\ \\ \text{Cl} \\ \\ \text{C}=\text{CH}_2 \end{array} \right]$	3,4-Polychloroprene	Poly[1-(1-chlorovinyl)ethylene]

^aIUPAC, International Union of Pure and Applied Chemistry.

Having two such nomenclature systems may be confusing at first. The source-based system is still the one of choice among most polymer chemists, notwithstanding the fact that such important reference works as *Chemical Abstracts* and *Polymer Handbook* have adopted the IUPAC system. The IUPAC is not dogmatic on the point; it recognizes the use of source-based names where no ambiguity arises, but it advocates a more systematic approach.

TABLE 1.3. Representative Nomenclature of Nonvinyl Polymers

Monomer Structure	Monomer Name	Polymer Repeating Unit	Source or Common Name	IUPAC Name
Polyethers				
	Ethylene oxide	$[-CH_2CH_2O-]$	Poly(ethylene oxide)	Poly(oxyethylene)
$HOCH_2CH_2OH$	Ethylene glycol	$[-CH_2CH_2O-]$	Poly(ethylene glycol)	Poly(oxyethylene)
CH_3O	Formaldehyde	$[-CH_2O-]$	Polyformaldehyde	Poly(oxymethylene)
CH_3CHO	Acetaldehyde	$[-CH(O)CH_3-]$	Polyacetaldehyde	Poly(oxyethylidene)
Polyesters				
	β -Propiolactone	$[-OCH_2CH_2C(=O)-]$	Poly(β -propiolactone) or poly(3-propionate)	Poly[oxy(1-oxopropane-1,3-diyl)]
$HO(CH_2)_9CO_2H$	10-Hydroxydecanoic acid	$[-O(CH_2)_9C(=O)-]$	Poly(10-decanoate)	Poly[oxy(1-oxodecane-1,10-diyl)]
$HOCH_2CH_2OH$ + 	Ethylene glycol + Terephthalic acid	$[-OCH_2CH_2OC(=O)C_6H_4C(=O)-]$	Poly(ethylene terephthalate)	Poly(oxyethylene-oxyterephthaloyl)

Polyamides

	Caprolactam	$[-NH(CH_2)_5C(=O)-]$	Polycaprolactam or nylon 6	Poly[imino(1-oxohexane-1,6-diyl)]
$H_2N(CH_2)_{10}CO_2H$	11-Aminoundecanoic acid	$[-NH(CH_2)_{10}C(=O)-]$	Poly(11-undecanoamide) or nylon 11	Poly[imino(1-oxoundecane-1,11-diyl)]
$H_2N(CH_2)_6NH_2$ + $HO_2C(CH_2)_8CO_2H$	Hexamethylenediamine + Sebacic acid	$[-NH(CH_2)_6NHCO(CH_2)_8C(=O)-]$	Poly(hexamethylene sebacamide) or nylon 610	Poly(iminohexane-1,6-diyliminosebacoyl)
	Terephthaloyl chloride + m -Phenylene-diamine	$[-NH-C_6H_4-NHC(=O)-C_6H_4-C(=O)-]$	Poly(m -phenylene-terephthalamide)	Poly(imino-1,3-phenylene-iminoterephthaloyl)
$H_2N(CH_2)_4NH_2$ + 	Tetramethylene diamine + m -Benzenedisulfonyl chloride	$[-NH(CH_2)_4NHOS_2-C_6H_4-SO_2-]$	Poly(tetramethylene- m -benzenesulfonamide)	Poly(sulfonyl-1,3-phenylene-sulfonylimino-butane-1,4-diylimino)

Solute	Solvent	Concentration g/100 ml	M_n
Insulin	Water		12,000; 36000, 48000
Pepsin	Water		36000
Excelsin	Water		214,000
Edesine	Water		50,000
Polyisobutylene			
C (-3-3.5)	C_6H_6	1.0	970,000
C (-3.5-4)	C_6H_6	0.5	970,000
	C_6H_6	1.0	625,000
C (4-5-5.5)	C_6H_{12}	0.5	608,000
	C_6H_{12}	1.0	408,000
4 (5.5-6.5)	C_6H_{12}	0.5	378,000
	C_6H_{12}	1.5-0.5	304,000
5 (6.5-8)	C_6H_{12}	1.0	308,000
6 (10-12)	C_6H_{12}	1.0	98,400
			99,200; 98,800

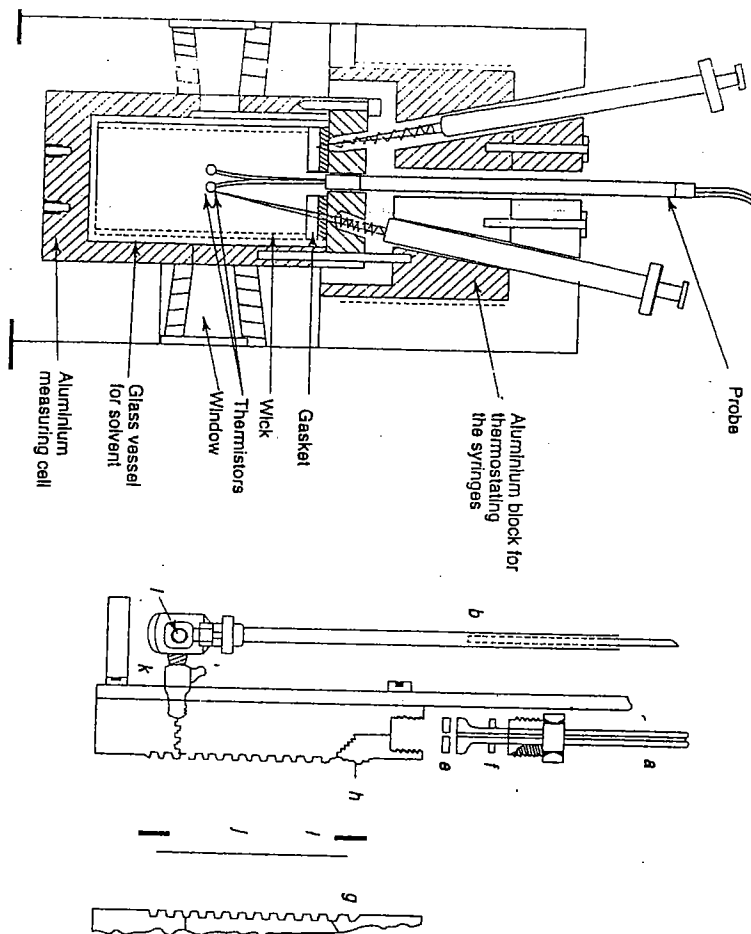


Fig. 9.22(b) Schematic diagram of a vapour pressure osmometer. (Courtesy: Knauer & Co., Berlin.)

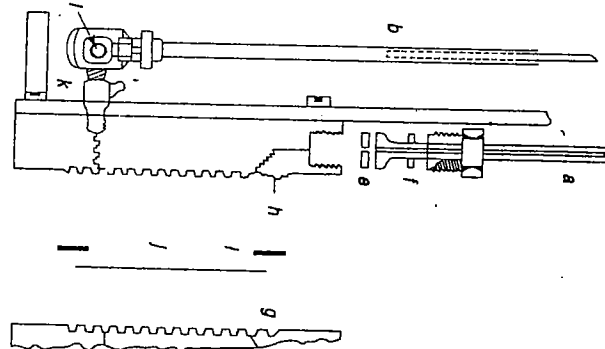


Fig. 9.23

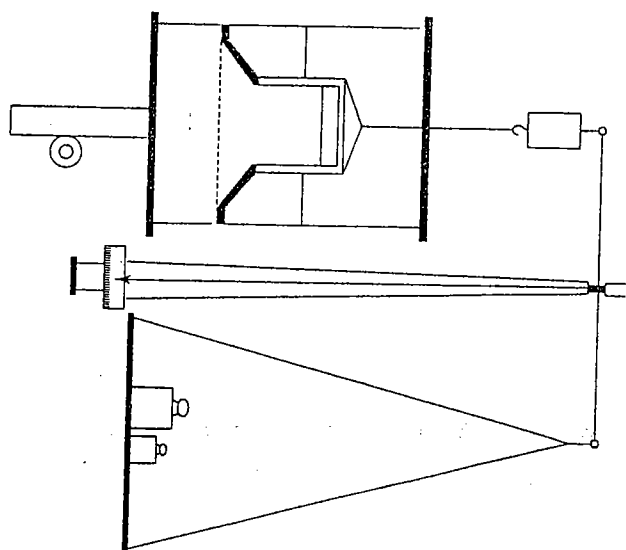


Fig. 9.24

Light Scattering Method

It was at first believed that the light is scattered only by particles of colloidal size and media free from such particles is known as optically empty. It has now been established that no matter how pure the fluid (gas or liquid) is, it is capable of scattering light. Light scattering is caused by centres due to clusters or associate formation.

Rayleigh observed the scattering by gas molecules and the intensity of the light scattering by isotropic (having the same property in all the directions) particles or clusters depends on their size, concentration and polarizability.

Tyndall noted that white light on being scattered by turbid medium gives reddish colour on transmission and bluish colour on polarization. Blue colour is scattered to greater extent than the red colour. This explains the effects of blue of the sky and red of sun set.

Debye⁴⁴ and others⁴⁵⁻⁴⁹ extended the theory of Rayleigh to non-ideal solutions of polymers and proteins. Bouguer-Lambert derived a law for the absorption of light. On similar grounds

$$I = I_0 \exp (-\tau x) \quad (9.75)$$

where I_0 and I are the intensities of incident and scattered beams respectively, τ is the turbidity and x is the thickness of the medium. The coefficient of scattering $R = \frac{I}{I_0} \frac{r^2}{\mu}$

where r is the distance from scattering volume to observer and v is the scattering volume. Barrow⁵⁰ has proved that for non-polarized incident radiations,

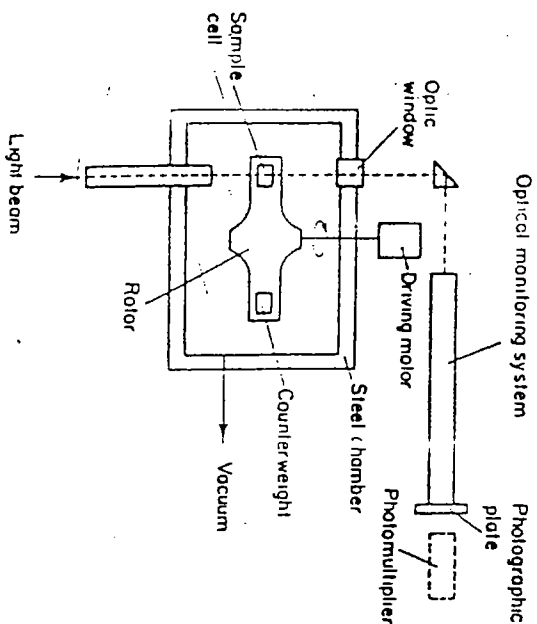


Figure 2.7. Schematic of an ultracentrifuge. [From Rabek,²⁶ copyright 1980. Reprinted by permission of John Wiley & Sons, Ltd.]

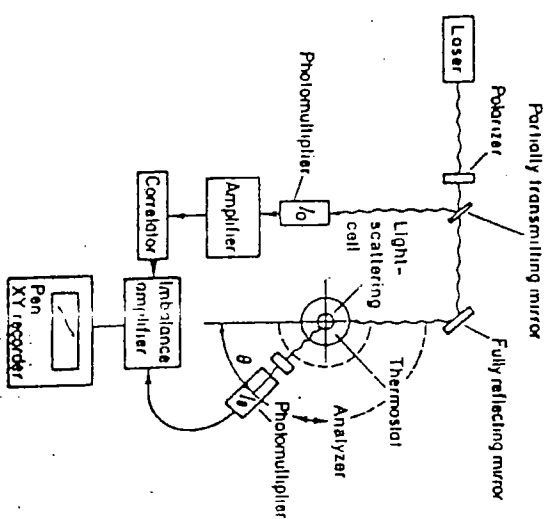


Figure 2.6. Schematic of a laser light-scattering photometer. [From Rabek,²⁶ copyright 1980. Reprinted by permission of John Wiley & Sons, Ltd.]

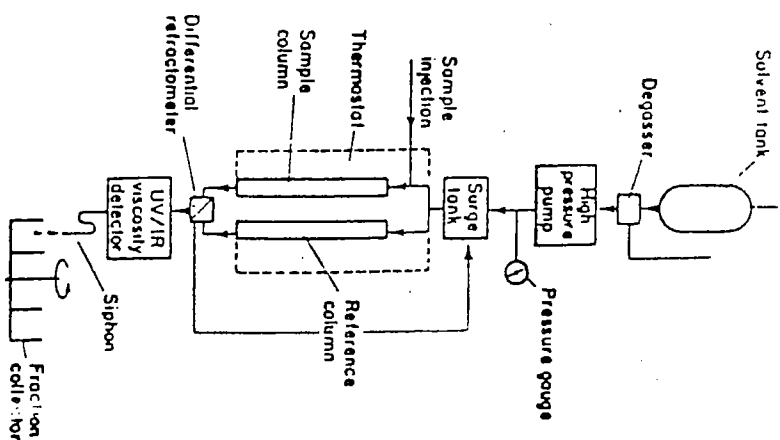


Figure 2.9. Schematic representation of a gel permeation chromatograph. [From Rai copyright 1980. Reprinted by permission of John Wiley & Sons, Ltd.]

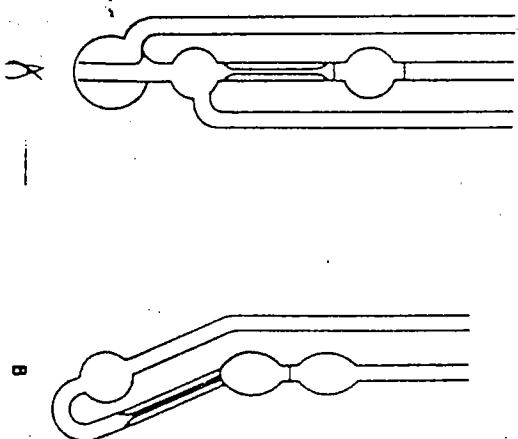
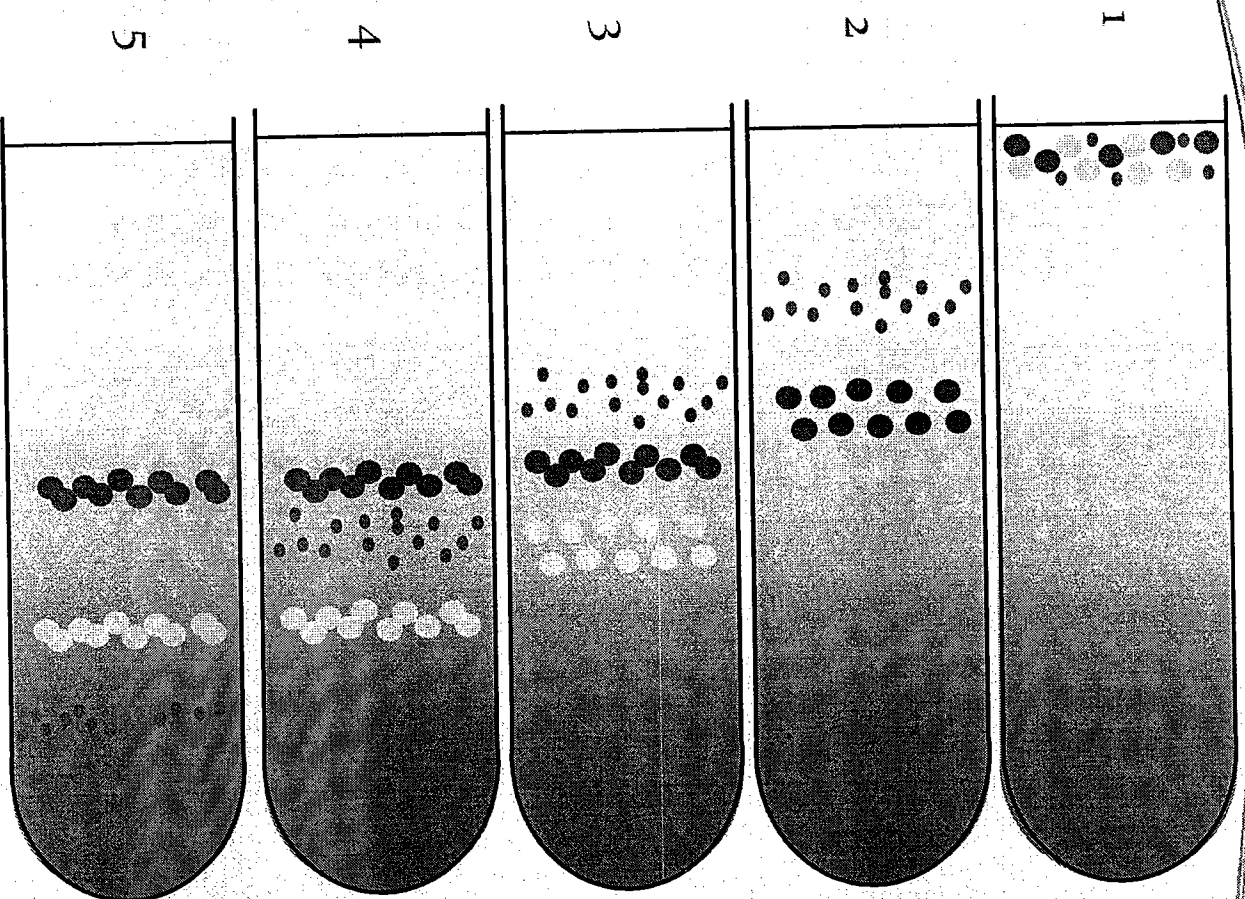


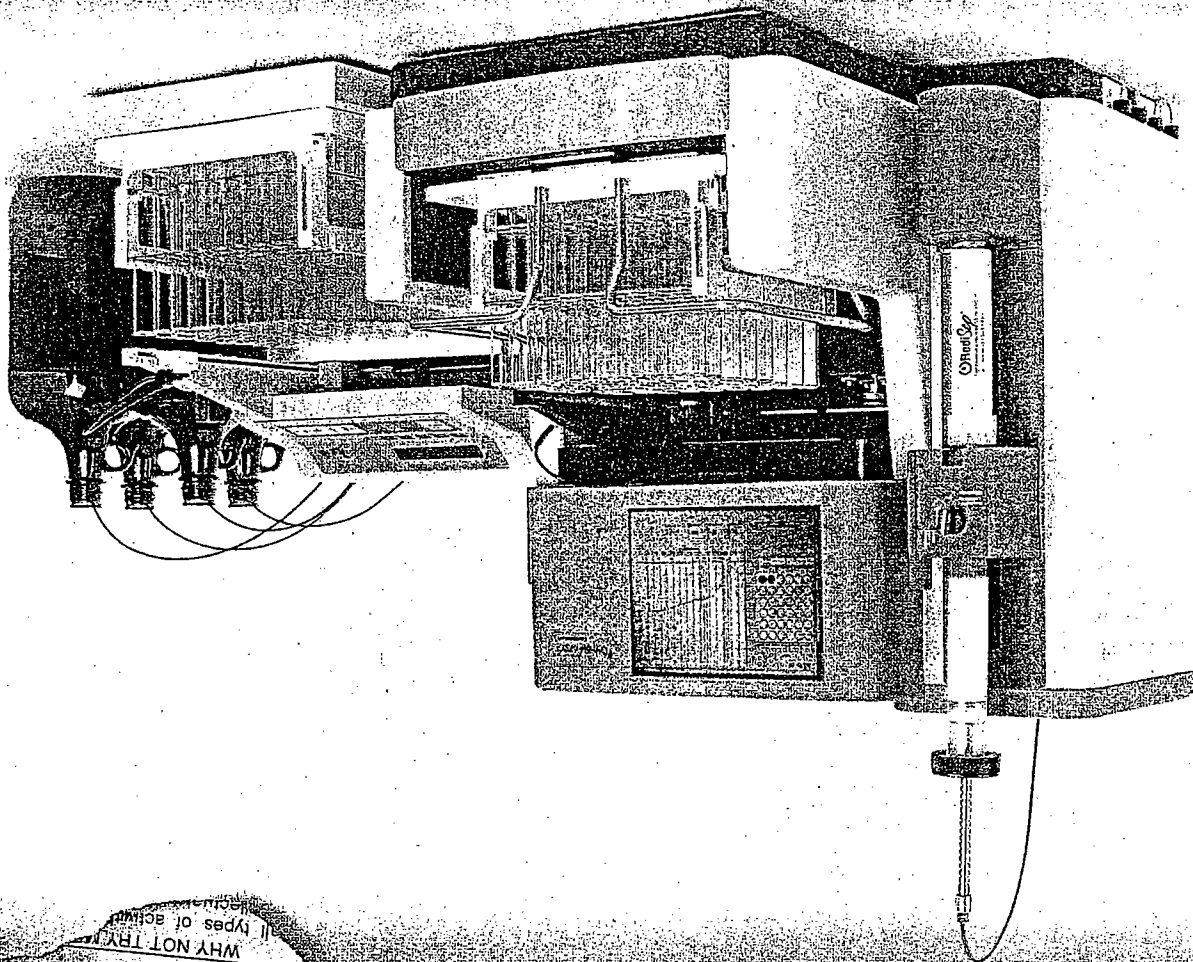
FIG. 2.8. (A) Unbehode, and (B) Cannon-Fenske.



Equilibrium
density banding

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Attractive, intelligent, quiet and hard working. 55923
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All types of activities



Speed • Performance • Reliability

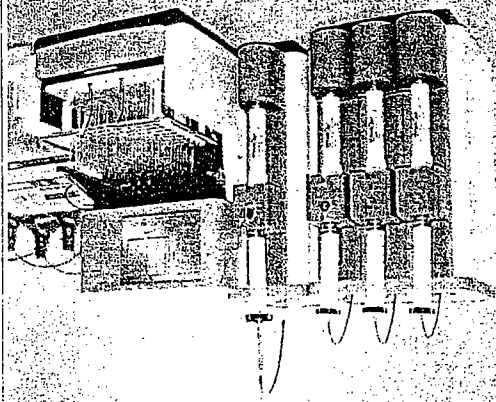
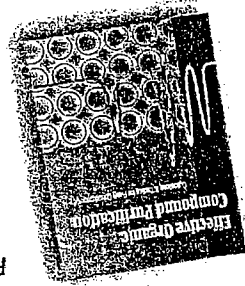
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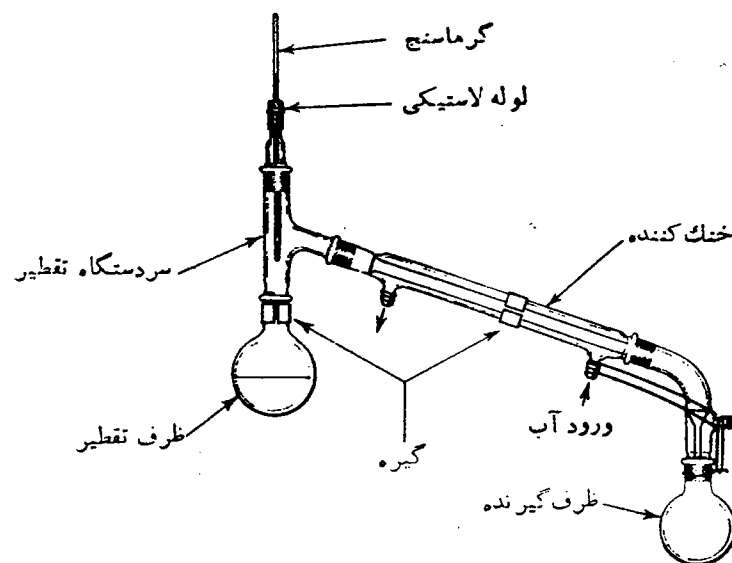
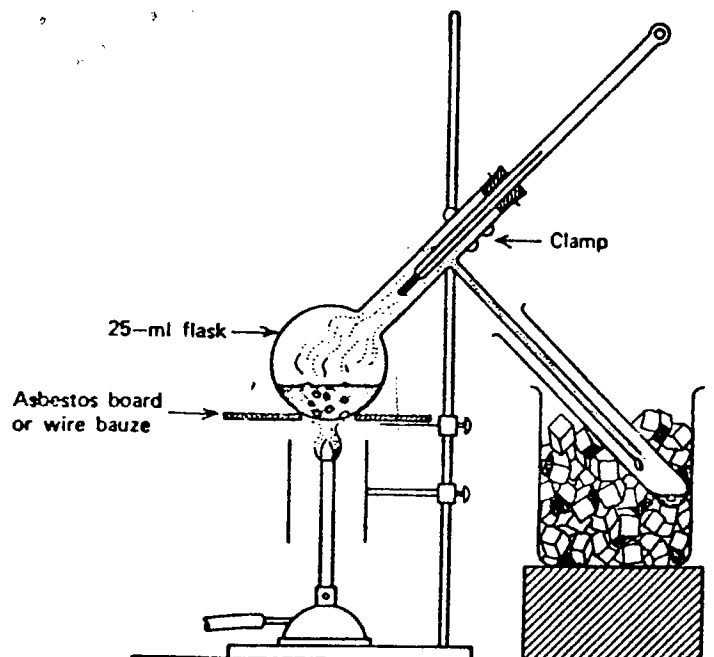
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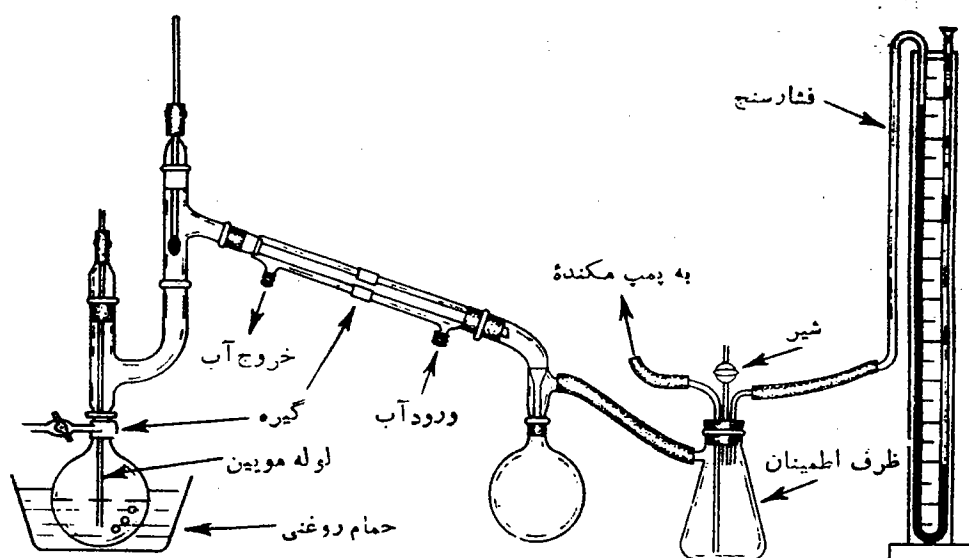


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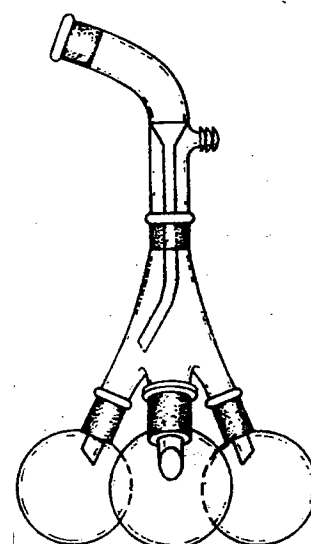
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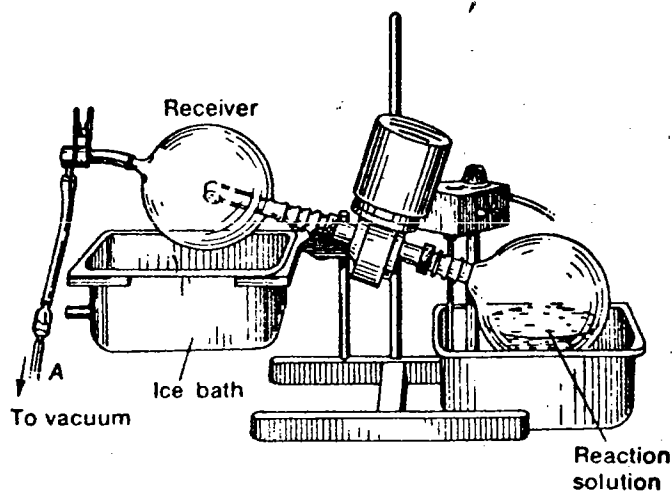
شکل ۲-۲ دستگاه معمولی تقطیر ساده، فشار آتمسفر یا خلا



شکل ۲-۸ دستگاه نمونه برای تقطیر در فشار کم



شکل ۲-۹ گیرنده چندظرفی برای تقطیر در خلا



Rotary Evaporator

(a)

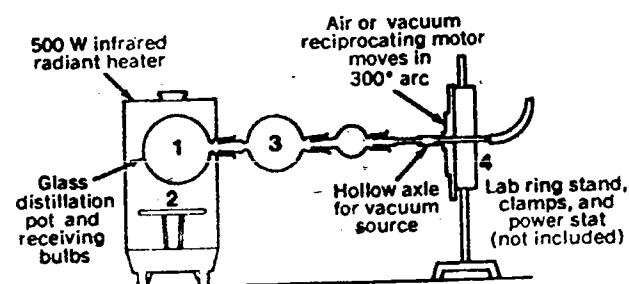


Figure 7.9. Kugelrohr distillation apparatus.

شکل ۱۸-۲ مول بخار ظرفی که در آن بخار در ابتدا تا نیمه با آب پر شده و قبل از گرم کردن به آن سنگ بزرگ جوی میزنند. چنانچه بخار با سرعت بسیار زیاد می‌رود، لوله اطراف آن فشار داخلی را کاهش می‌دهد.

شکل ۱۱-۲ دستگاه تقطیر با بخار آب در صورتی که بخار در داخل ظرفی بزرگ می‌شود، به جای لوله طولانی، خوب می‌شود. بخار از آنجا می‌رود.

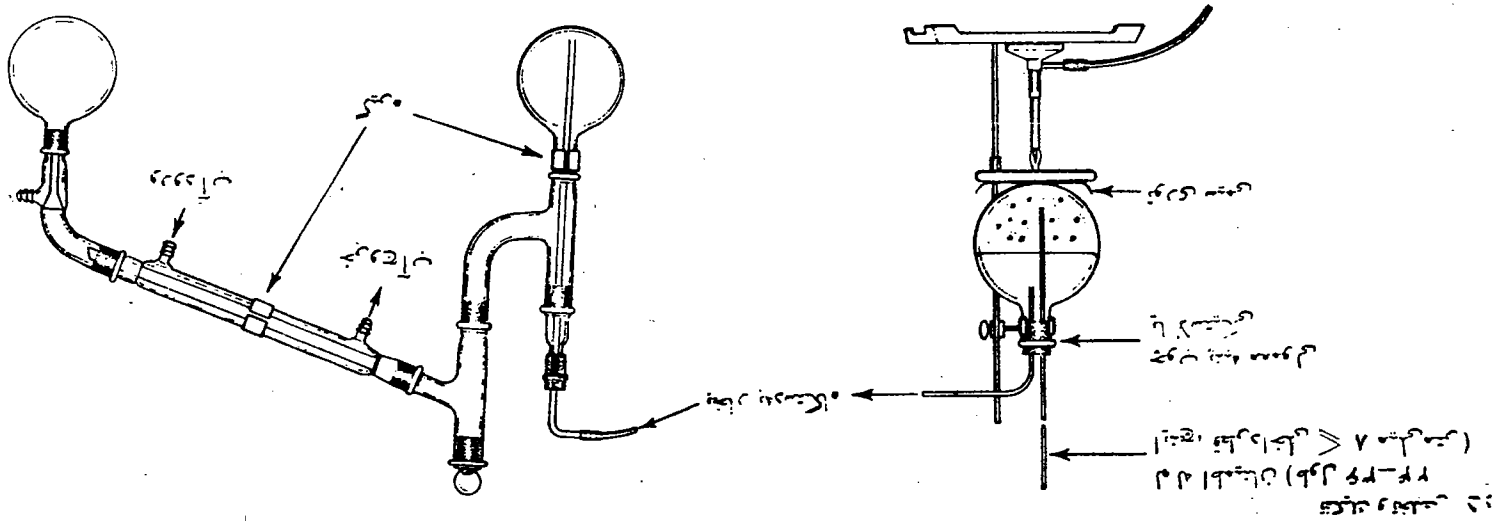


Fig. 1.104

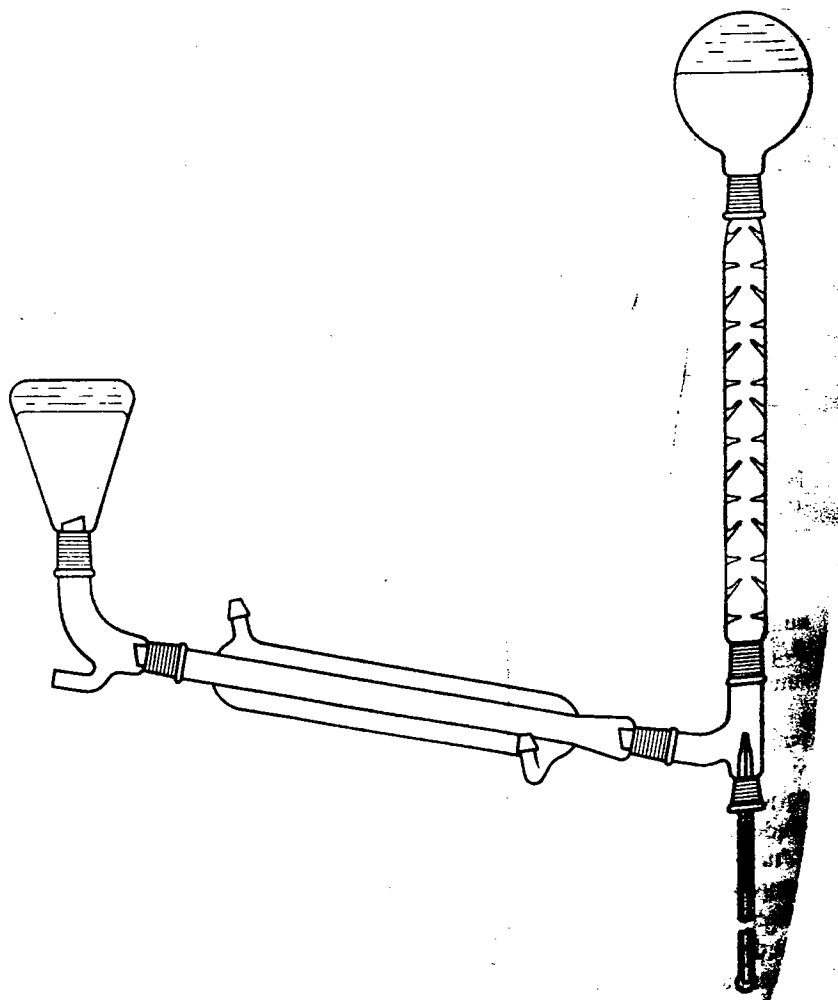
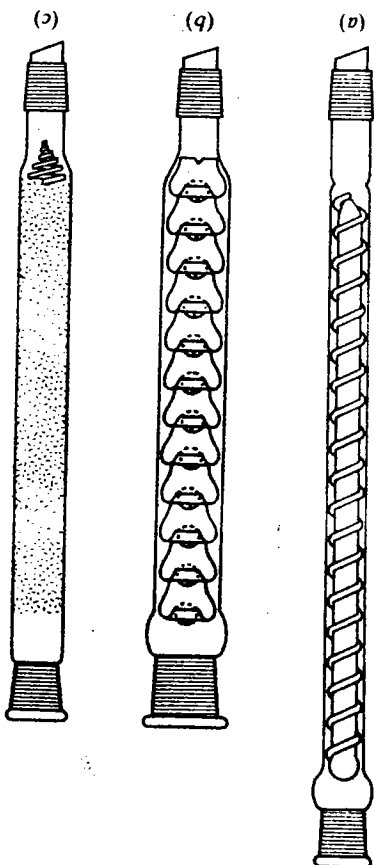
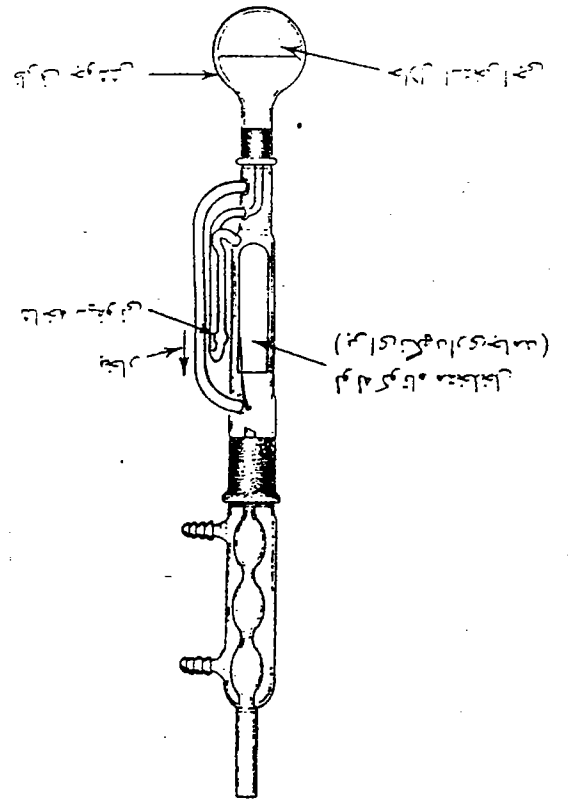


Fig. 1.105

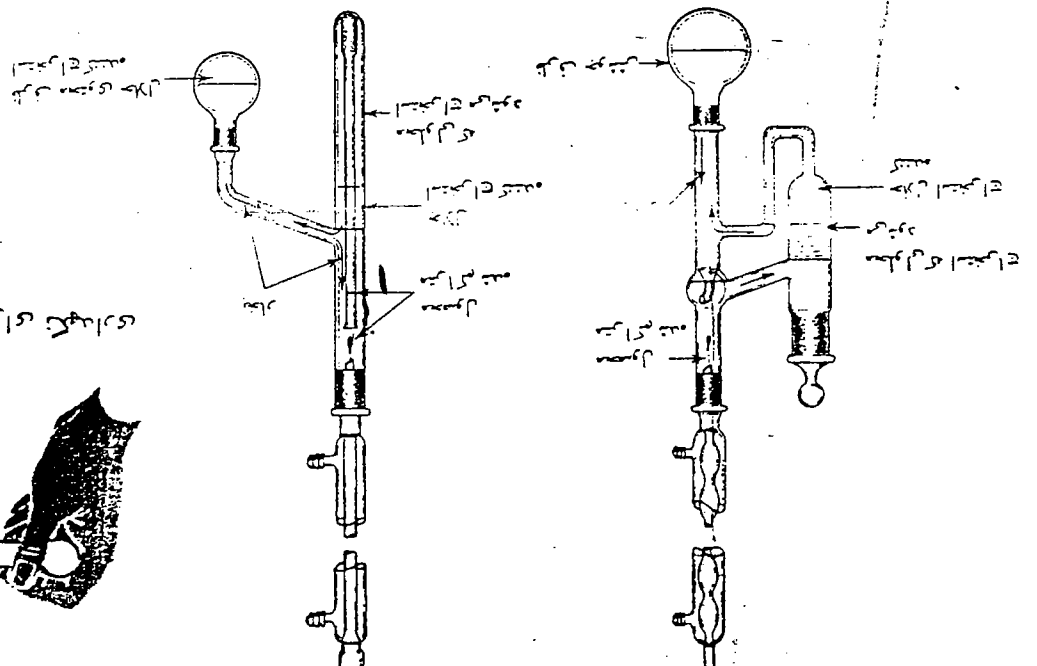


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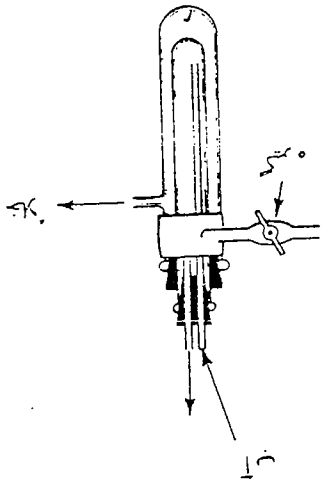
شکل ۳-۴ دستگاه استخراج مویکله



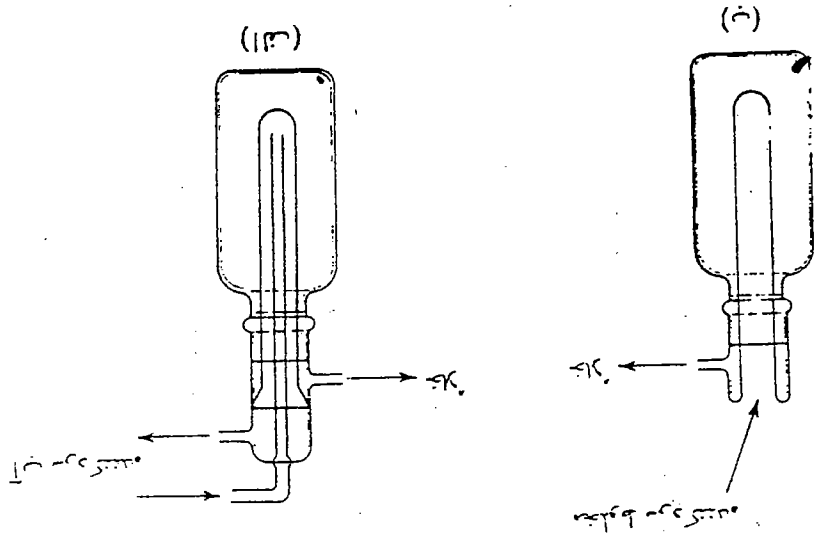
شکل ۳-۵ دستگاه استخراج مویکله



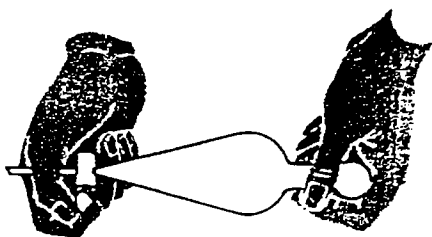
شکل ۳-۶ دستگاه استخراج مویکله



شکل ۳-۷ دستگاه استخراج مویکله



شکل ۳-۸ روش مناسب برای نگهداری دستگاه



The spectra depicted in this chapter (^1H nmr, ^{13}C nmr, ir, uv-vis, and ms) were all obtained using pure substances. It is much more common, however, to encounter an organic substance, either formed as the product of a chemical reaction or isolated from natural sources, as but one component of a mixture of two or more compounds. Just as the last half of the twentieth century has seen a revolution in the methods available for the identification of organic compounds, so too has it seen remarkable advances in methods for their separation and purification.

Classical methods for separation and purification include fractional distillation of liquids and recrystallization of solids, and these two methods are routinely included in the early portions of laboratory courses in organic chemistry. Because they are capable of being adapted to work on a large scale, fractional distillation and recrystallization are the preferred methods for purifying organic substances in the pharmaceutical and chemical industries.

Some other methods are more appropriate to the separation of small amounts of material in laboratory-scale work and are most often encountered there. In-deed, it is their capacity to deal with exceedingly small quantities that is the strength of a number of methods that together encompass the various forms of chromatography. The first step in all types of chromatography involves adsorbing the sample onto some material called the *stationary phase*. Next, a second phase (the *mobile phase*) is allowed to move across the stationary phase. Depending on the properties of the two phases and the components of the mixture, the mixture is separated into its components according to the rate at which each is removed from the stationary phase by the mobile phase.

In gas chromatography (GC) the stationary phase consists of beads of an inert solid support coated with a

high-boiling liquid, and the mobile phase is a gas, usually helium. Figure 13.41 is a diagram showing the construction of a typical gas chromatograph. The sample is injected by syringe onto a heated block where a stream of helium carries it onto a coiled column packed with the stationary phase. The components of the mixture move through the column at different rates. They are said to have different *retention times*. Gas chromatography is also referred to as *gas-liquid partition chromatography*, because the technique depends on how different substances partition themselves between the gas phase (dispersed in the helium carrier gas) and the liquid phase (dissolved in the coating on the beads of solid support).

Typically the effluent from a gas chromatograph is passed through a detector which feeds a signal to a recorder whenever a substance different from pure carrier gas leaves the column. Thus one determines the number of components in a mixture by counting the number of peaks on a strip chart. It is good practice to carry out the analysis under different conditions by varying the liquid phase, the temperature, and the flow rate of the carrier gas so as to ensure that two substances have not eluted together and given a single peak under the original conditions. Gas chromatography can also be used to identify the components of a mixture by comparing their retention times with those of authentic samples.

In gas chromatography-mass spectrometry (GC/MS), the effluent from a gas chromatograph is passed into a mass spectrometer and a mass spectrum is taken for each peak. Thus gas chromatography is used to separate a mixture and mass spectrometry is used to analyze it. Gas chromatography-mass spectrometry is a very powerful analytical technique. One of its more visible applications involves the testing of athletes for steroids, stimulants, and other performance-enhancing drugs. These drugs are converted in the body to derivatives called *metabolites* which are then excreted in the

urine. When the urine is subjected to GC/MS analysis, the mass spectra of its organic components are identified by comparison with the mass spectra of known metabolites stored in the instrument's computer. Using a similar procedure, the urine of newborn infants is monitored by GC/MS for metabolite markers of genetic disorders that can be treated if detected early in life. Gas chromatography-mass spectrometry is also used for more routine analyses such as detecting and measuring the concentration of halogenated hydrocarbons in drinking water.

While GC/MS is the most widely used analytical method that combines a chromatographic separation with the identification power of mass spectrometry, it should be apparent that it need not be the only one. Chemists have coupled mass spectrometers to most of the instruments that are used to separate mixtures. Perhaps the ultimate is mass spectrometry-mass spectrometry (MS/MS), in which one mass spectrometer generates and separates the molecular ions of the components of a mixture and a second mass spectrometer examines their fragmentation patterns!

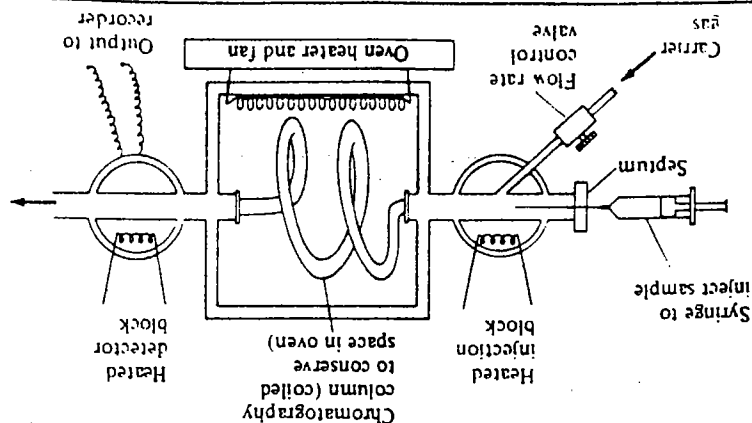


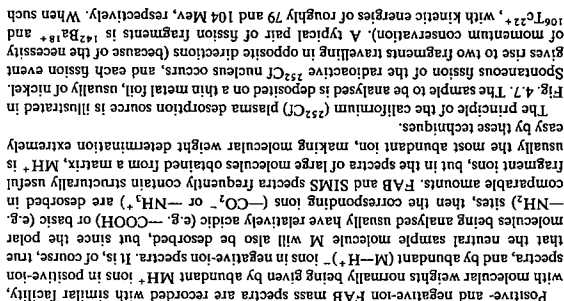
FIGURE 13.41 Diagram of a gas mass spectrometer. When connected to a chromatograph, as in GC/MS, the effluent is split into two streams as it leaves the column. One stream goes to the detector, the other to the mass spectrometer. (Adapted from H. D. Durst and G. W. Gokel, *Experimental Organic Chemistry*, 2d ed., McGraw-Hill, New York, 1987.)

(7) $\left[\frac{1}{\rho} + \left(1 + \frac{\rho}{\sigma} \right)^2 \right]^{-1}$ are desorbed along with the sample ions, and may serve to mass mark the specimen.

It is important that the sample should dissolve in the matrix, and preferably be more hydrophobic than the matrix so that it will occupy the matrix/vacuum interface. This is desirable because the x-ray beam only penetrates about 0.1 μm into the matrix. A commonly used alternative matrix to glycerol is thioglycerol/ H_2O (1 : 1).[†] More hydrophobic matrices which may on occasions be used to advantage are tetragol (3) and terecol (4).

$\begin{array}{c} \text{(3)} \\ \text{HO(CH}_2\text{CH}_2\text{CH}_2\text{O)}_n\text{H} \end{array}$

$\begin{array}{c} \text{(4)} \\ \text{HO(CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{O)}_n\text{H} \end{array}$

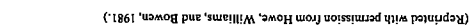


CF Rfission

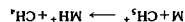
Sample

Ni foil (10^{-3} mm)

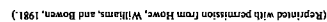
+ or -



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$$M + CH_5 + MH \rightleftharpoons MCH_5 + H_2$$
$$M + CH_5 + MH \rightleftharpoons CH_4 + M$$


source is given in Fig. 4.4.



Although EI does not produce satisfactory negative-ion spectra, negative-ion C₆₀ works well for molecules with electron-accepting properties (e.g., trifluoroacetates equilibrate, and nitro-compounds). This is because the collisions occurring in a C₆₀ source reduce the large initial kinetic energies of the bombarding electrons to low

$$M + CH_3O^- \longrightarrow (M-H)^- + CH_3OH$$

Brominated base by abstracting a proton from the sample molecule.

as it is CH_3OH can be captured to give a radical anion. Alternatively, a reagent ion such as CH_3O^- may be generated in the C.I. source. This can then act as a

Field description. In this technique, the probe tip shown in Fig. 4.2 is replaced by a thin (e.g. 5 μm) wire on which sharp needles have been grown. The wire is supported between two posts on the probe (Fig. 4.5a).

(a) Cathode slit

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A solution of a small amount of sample (e.g. 1 μ g) is deposited on the wire. In the mass spectrometer, the wire is maintained at +8 kV, and can be heated. Since the field at their tips may be as high as

vacant orbitals of the metal from which the wire is made. Thus, positive ions (M^+) are created at the positive wire, and M^+ is largely desorbed by Coulombic repulsion (Fig. 4.5b) often with some help from limited heating of the wire. In this way M^+

sample pressure at the end of a needle may be remarkably high due to the strong electric fields pertaining there. As a consequence, bimolecular reactions may occur, and field-assisted (FA) reactions may be observed. This is the case with the

Desorption ionization by particles or radiation. Between the late 1970s and the present time, four methods have been developed which allow in many cases the molecular

are, at the present time, more widely used than the IUPAC-recommended names. (The latter were adopted by the IUPAC to avoid inconsistencies arising from "viscosity" designations where there were no units of viscosity.) *Relative viscosity* (viscosity ratio) (η_{rel}) is the ratio of solution viscosity to solvent viscosity, which is proportional to a first approximation for dilute solutions to the ratio of the corresponding flow times. Viscosity units (commonly expressed as poises) or flow times cancel out in the various viscosity expressions. *Specific viscosity* (η_{sp}) is the fractional increase in viscosity. Both η_{rel} and η_{sp} are dimensionless. As concentration increases, so does viscosity. Hence to eliminate concentration effects, the specific viscosity is divided by concentration and extrapolated to zero concentration to give the *intrinsic viscosity*, $[\eta]$. Not uncommonly viscosities are determined at a single concentration and the *inherent viscosity* (η_{inh}) is used as an approximate indication of molecular weight. Inherent viscosity extrapolates to the same $[\eta]$. Concentration, C , in the above expressions is in grams per 100 mL of solvent or in grams per cubic centimeter, more commonly the former. Thus reduced, inherent and intrinsic viscosities have units of deciliters per gram or, less commonly, cubic centimeters per gram. Obviously, units of concentration must be specified when viscosity data are reported.

Intrinsic viscosity is the most useful of the various viscosity designations because it can be related to molecular weight by the Mark-Houwink-Sakurada equation:

$$[\eta] = KM_v^a$$

Table 2.2. Dilute solution viscosity designations^a

Common name	IUPAC name	Definition
Relative viscosity	Viscosity ratio	$\eta_{rel} = \frac{\eta}{\eta_0} = \frac{l_0}{l}$
Specific viscosity	—	$\eta_{sp} = \frac{\eta - \eta_0}{c} = \frac{l_0 - l}{l_0} = \frac{\eta_{rel} - 1}{\eta_{rel}}$
Reduced viscosity	Viscosity number	$\eta_{red} = \frac{C}{\eta_{sp}} = \frac{C}{\eta_{rel} - 1}$
Inherent viscosity	Logarithmic viscosity number	$\eta_{inh} = \frac{C}{\ln \eta_{rel}}$
Intrinsic viscosity	Limiting viscosity number	$[\eta] = \lim_{C \rightarrow 0} \left(\frac{C}{\eta_{sp}} \right) = (\eta_{inh})_{C=0}$

^a Concentrations (most commonly expressed in grams per 100 mL of solvent) of about 0.5 g/dL.

5- 5
4- 5
3-
2-
1-

Brookfield Viscosity, Brookfield Viscometers, Measurements & Specifications

Brookfield Viscosity Explained



Brookfield viscosity usually refers to a viscosity measurement performed with a Brookfield Viscometer, sometimes referred to as a Brookfield viscosimeter. There are several models of viscometer available from Brookfield but the majority operate in the same manner: the viscometer motor rotates the spindle at a defined speed (measured in rpm) or shear rate and the viscometer measures the resistance to rotation and reports a viscosity value. Various spindle designs can be employed, depending on the nature of the sample and the requirements. Here is a brief introduction to the most popular arrangements:

Dip-in LV Spindles & RV Spindles

Labelled as LV or RV spindle sets, these comprise simple shafts ending in a disk or cylinder. A sample of 400 - 600ml in a suitable container is placed under the viscometer which is then lowered to dip the spindle into the sample up to an immersion mark on the spindle shaft. The dip-in spindle is suitable for comparative testing of the viscosity of free-flowing fluids.

Small Sample Adapter (SSA)

The Small Sample Adapter is a concentric cylinder measuring system, often known as a coaxial or "cup and bob" system. In the small sample adapter a small sample (typical only 5 - 10ml) is sheared between the moving inner cylinder and stationary outer cylinder or chamber. The accessory was, as its name suggests, originally designed for measuring samples of limited quantity however due to its fairly narrow clearances the system operates in a degree of defined shear - a valuable capability of you wish to perform viscosity / shear rate profiles on a sample.

Ultra Low Adapter (ULA)

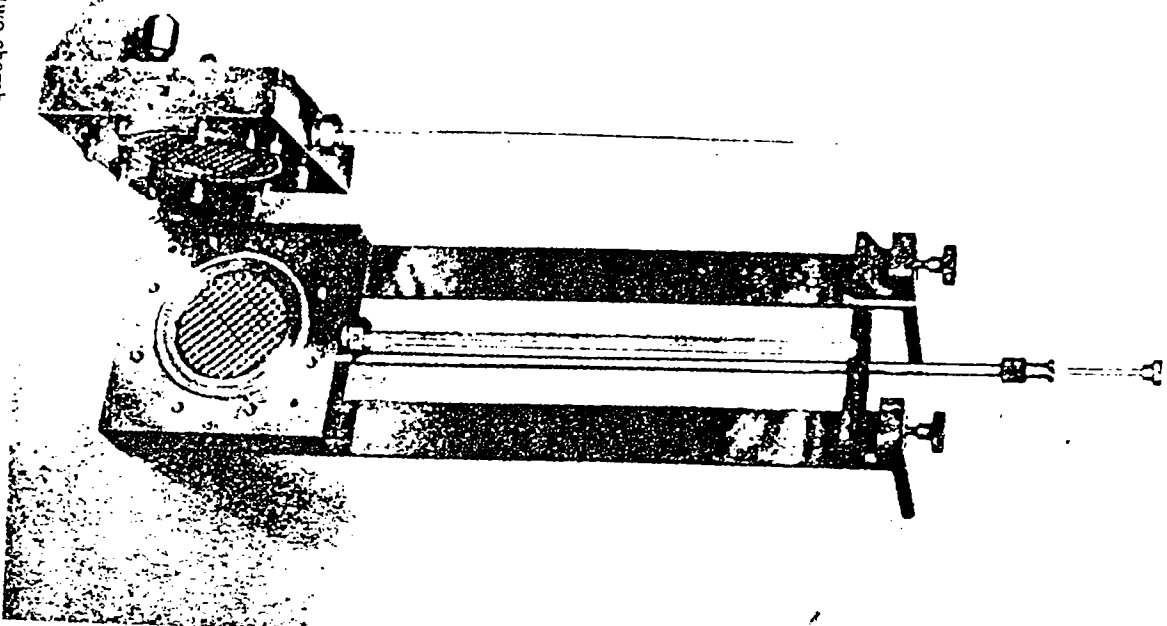


Figure 3.4 A two-chamber osmometer used by Krigbaum and Flory. (Reprinted from P. J. Flory, *Principles of Polymer Chemistry*; Copyright © 1953 by Cornell University. Used by permission of the publisher, Cornell University Press.)

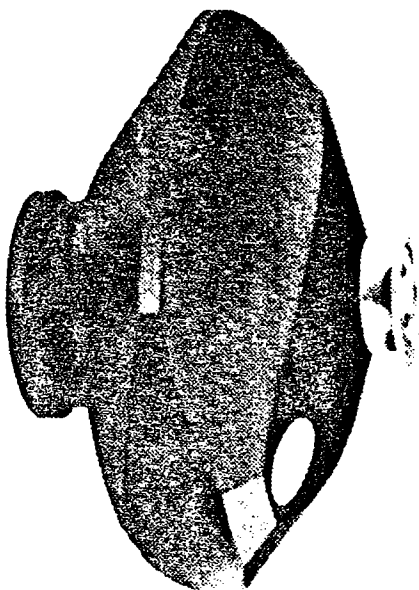


Figure 3.5 A two-cell rotor used in the Spinco model E ultracentrifuge. (Reprinted from Mario Zeller, *Model E Analytical Ultracentrifuge: Instruction Manual*. Used by permission of Beckman Instruments, Inc.)

run. Centrifuges are designed to run at speeds of 2000–68,000 rpm. The lower limit is given by the requirement of mechanical stability of the rotor, the upper limit by engineering properties of the construction materials.

The heart of the ultracentrifuge is a rotor (Figure 3.5). It is made from materials having the best strength-to-mass ratio: aluminum and, more recently, titanium. At a distance of about 6 cm from the axis, it has two holes for a cell and a counterbalance (recently, rotors with up to eight holes have become available, allowing multicell runs). The cell (Figure 3.6) consists of a housing, a centerpiece that forms the body of the solution compartment, and two thick (5 mm) windows that form the sides of the cell and allow for optical observation. The windows should not distort excessively under the action of centrifugal forces. Originally, they were made from fused quartz, but this material proved to be too soft. Sapphire windows are preferred for more demanding applications.

The centerpiece has either one or two compartments. In the latter case, one compartment is filled with the macromolecular solution and the other with reference solvent. The compartments are sector shaped with the apex at the rotor axis. This arrangement allows for undisturbed radial movement of molecules in the vicinity of the walls. The twin compartments can each hold up to 0.45 mL of liquid, forming a liquid column up to 10 mm long.

The rotor spins in a cylindrical chamber. Now, the centrifugal forces are huge (with accelerations equivalent to up to 200,000 times gravity), and the kinetic

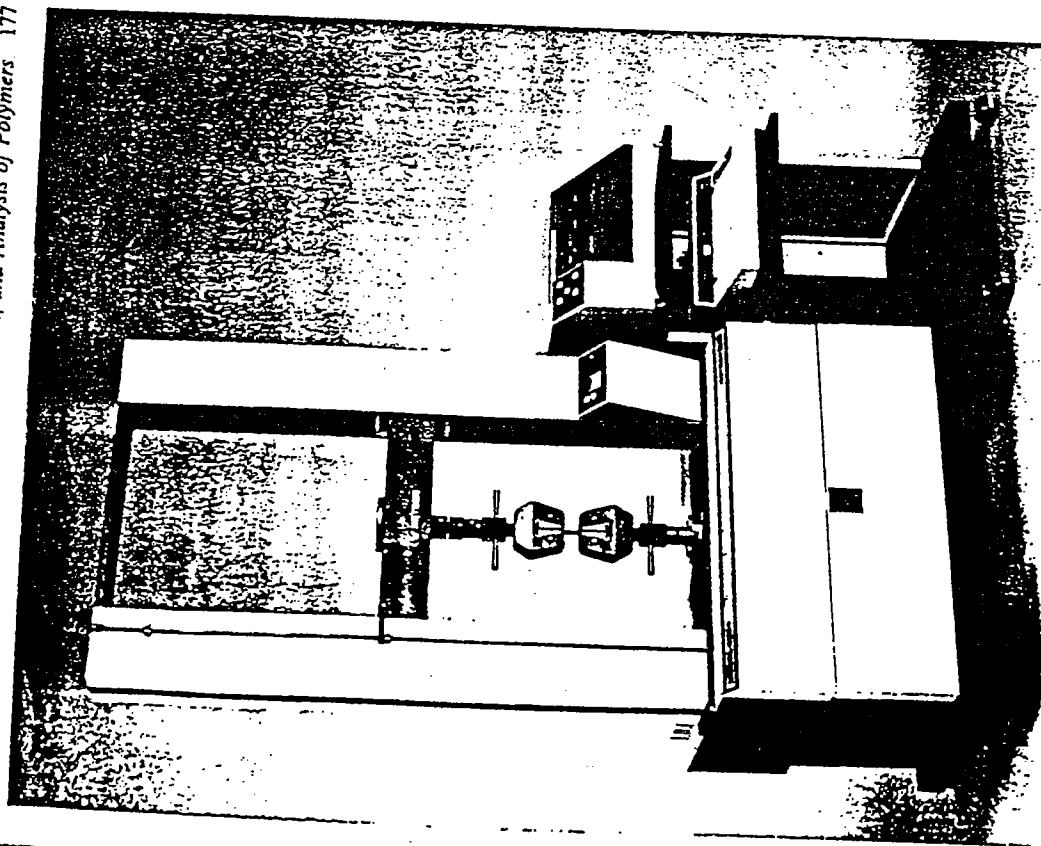


Figure 5.22. Instrument for performing tensile, compression, shear, and flexural testing. Shown with tensile testing grips and sample. [Courtesy of Instron Corp.]

and flexural strengths. Repeated flexing of a sample through a given distance often causes the sample to fail at lower stress than it would for a single flexure, a phenomenon known as *fatigue*.^{44b} Alternating cycles of tensile and compressive stress are also used to evaluate fatigue. In general, fatigue resistance decreases as polymer rigidity or crosslinking increases.

Table 4.1. Mechanical properties of common homopolymers^a

Polymer	Tensile properties at break					Property
	Strength ^b (MPa)	Modulus ^b (MPa)	Elongation (%)	Compressive strength ^b (MPa)	Flexural strength ^b (MPa)	
Polyethylene, low density	8.3-31	172-283	100-650	—	—	No break
Polyethylene, high density	22-31	1070-1090	10-1200	20-25	—	0.23-2.3
Polypropylene	31-41	1170-1720	100-600	38-55	41-55	0.23-0.57
Poly(vinyl chloride)	41-52	2410-4140	40-80	55-90	69-110	0.23-1.3
Polystyrene	36-52	2280-3280	1.2-2.5	83-90	69-101	0.20-0.26
Poly(methyl methacrylate)	48-76	2240-3240	2-10	72-124	72-131	0.17-0.34
Polytetrafluoroethylene	14-34	400-552	200-400	12	—	1.7
Nylon 66	76-83	—	60-300	103	42-117	0.46-1.2
Poly(ethylene terephthalate)	48-72	2760-4140	50-300	76-103	96-124	0.14-0.37
Polycarbonate	66	2380	110	86	93	9.1

^aValues taken from Agronoff,^{44a} converted to SI units, and rounded off.

^bTo convert megapascals to pounds per square inch multiply by 145.

^cLead notched impact test (see Chap. 5). To convert newtons per centimeter to foot-pounds per inch, multiply by 1.75.



TABLE 2.2 Chain Transfer Constants for Selected Solvents at 60 °C with Respect to Polystyrene and Poly(vinyl acetate)

Solvent	Polystyrene	Poly(vinyl acetate)
$C_s \times 10^4$		
Benzene	0.18	2.2
Toluene	1.25	21
Ethylbenzene	6.7	55
Isopropylbenzene	8.2	90
n-Heptane	0.42	17
Acetone	4.1 (80 °C)	11
Butanone	5.0 (80 °C)	65
Ethyl acetate	—	2.3
Ethyl butyrate	—	17 (50 °C)
Phenol	—	220 (45 °C)
Anilin	—	210
n-Butyl chloride	0.04	10
n-Butyl bromide	0.06	50
n-Butyl iodide	1.85	800
Methylene chloride	0.15	4
Chloroform	0.5	140
Carbon tetrachloride	92	960
Carbon tetrabromide	13,600	39,000

We should now return to the relations predicting the degree of polymerization from kinetic considerations. In the presence of various types of transfer processes, equation (2.2.58) should be modified to

$$\overline{DP}_n = r_p / (r_{td} + r_{tr}/2 + r_{ti} + r_{tm} + r_{ts}) \quad (2.2.68)$$

Upon appropriate substitutions, this relation may be converted to

$$\frac{1}{\overline{DP}_n} = \frac{1}{\overline{DP}_0} + C_1 \frac{[M]}{[I_2]} + C_m + C_s \frac{[M]}{[SX]} \quad (2.2.69)$$

It is obvious that the degree of polymerization will be severely limited if any of the last three terms in equation (2.2.69) has a significant value. The first term can be minimized by selecting an initiator with low C_1 value and/or by keeping the initiator concentration low (and increasing temperature if a higher initiation rate is required). The last term can be minimized by avoiding solvents and impurities with significant values of C_s . However, the C_m term cannot be avoided: Monomers with high C_m cannot be polymerized to high molecular weights using radical polymerization techniques.

On the other hand, chain transfer can be utilized when reduction of degree of

Table 2.3. Representative viscosity-molecular weight constants^a

Polymer	Solvent	Temperature, °C	Molecular weight range $\times 10^{-4}$	$K^b \times 10^3$	a^b
Polystyrene (atactic) ^c	Cyclohexane	35 ^d	8-42 ^e	80	0.50
	Cyclohexane	50	4-137 ^e	26.9	0.599
	Benzene	25	3-61 ^f	9.52	0.74
Polyethylene (low pressure)	Decalin	135	3-100 ^e	67.7	0.67
Poly(vinyl chloride)	Benzyl alcohol	155.4 ^d	4-35 ^e	156	0.50
	Cyclohexanone	20 ^d	7-13 ^f	13.7	1.0
Polybutadiene					
98% <i>cis</i> -1,4, 2% -1,2	Toluene	30 ^d	5-50 ^f	30.5	0.725
97% <i>trans</i> -1,4, 3% -1,2	Toluene	30	5-16 ^f	29.4	0.753
Polyacrylonitrile	DMF ^g	25	5-27 ^e	16.6	0.81
	DMF	25	3-100 ^f	39.2	0.75
Poly(methyl methacrylate- co-styrene)					
30-70 mol %	1-Chlorobutane	30	5-55 ^e	17.6	0.67
71-29 mol %	1-Chlorobutane	30	4.8-81 ^e	24.9	0.63
Poly(ethylene terephthalate)	<i>m</i> -Cresol	25	0.04-1.2 ^f	0.77	0.95
Nylon 66	<i>m</i> -Cresol	25	1.4-5 ^f	240	0.61

^a Values taken from reference 4e.^b See text for explanation of these constants.^c Atactic defined in Chapter 3.^d θ temperature.^e Weight average.^f Number average.^g N,N-dimethylformamide.

to enhance the signal-to-noise ratio circumvent the low sensitivity arising from ^{13}C 's low abundance. Spectra may be simplified further by using a second radiofrequency to decouple the spin interactions of ^{13}C with neighboring protons, thus yielding singlet resonances for each carbon. Figure 5.4 shows high-resolution proton-decoupled ^{13}C spectra of polypropylene of varying tacticity. Fine structure in the spectra may again be correlated with pentad sequences,^{31,32} as discussed previously.

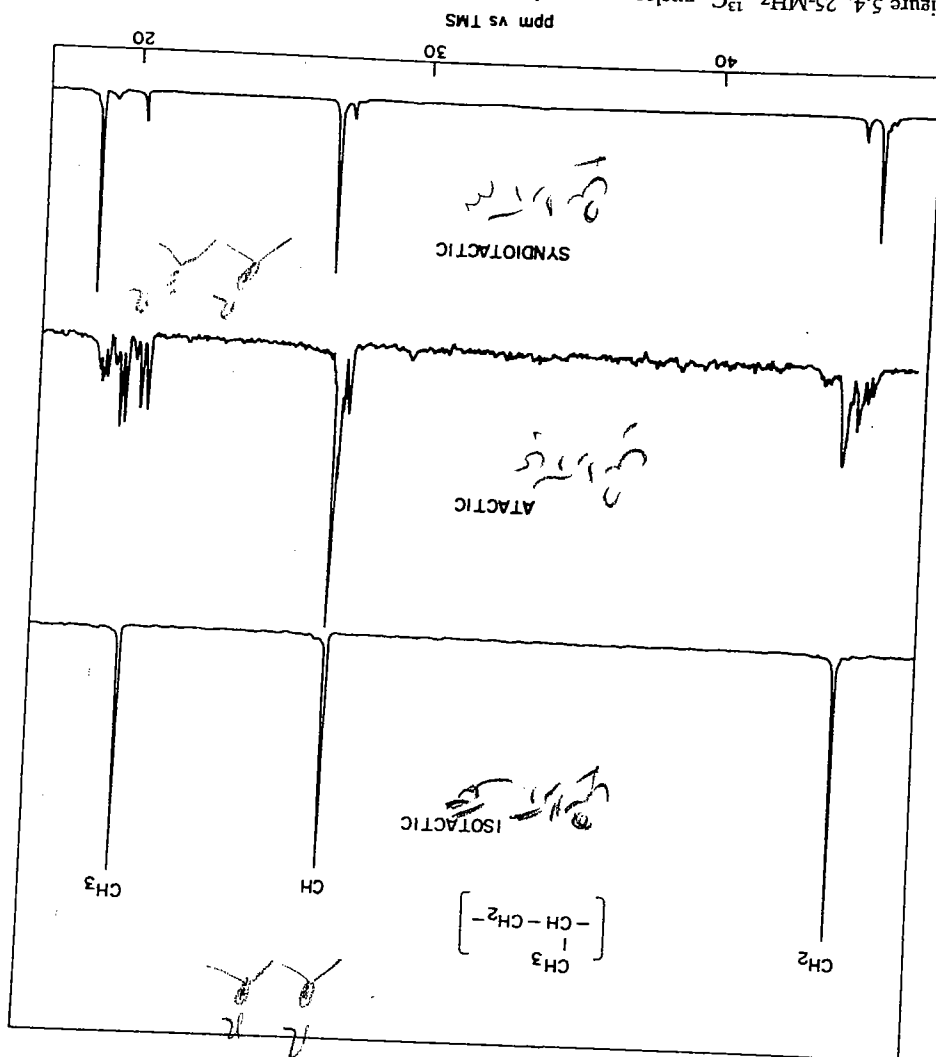
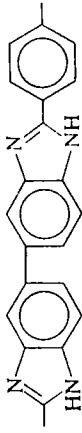
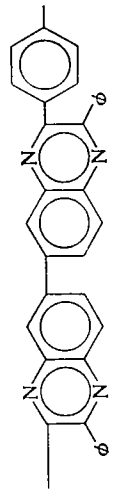
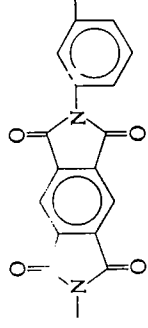
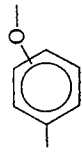
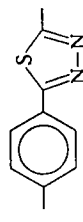
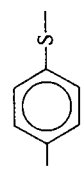
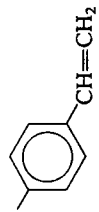
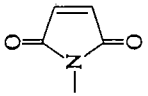
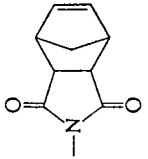


Figure 5.4. 25-MHz ^{13}C nuclear magnetic resonance spectrum of polypropylene (3.5% weight/volume in 1,2,4-trichlorobenzene at 135°C). [Courtesy of Dr. Frank Bovey, Bell Laboratories.]

4.3. Representative thermally stable polymers^a

Type	Structure	Decomposition temperature (°C) ^b
p-phenylene		660
enzimidazole		650
quinoxaline		640
oxazole		620
indole		585 ^c
phenylene oxide		570
thiadiazole		490
(phenylene sulfide)		490

^a from Korshak.¹⁵^b in vacuum atmosphere unless otherwise indicated.^c in vacuum atmosphere.Table 4.4. Reactive end groups for converting aromatic oligomers to network polymers^a

Type	Structure
Ethynyl	$\text{—C}\equiv\text{CH}$
Phenylethynyl	$\text{—C}\equiv\text{C}\phi$
Phenylbutadiynyl	$\text{—C}\equiv\text{C—C}\equiv\text{C}\phi$
Phenylbutenyne	$\text{—C}\equiv\text{C—CH=CH}\phi$
Biphenylene	
Styryl	
Maleimide	
Nadimide (5-norbornene-2,3-dicarboximide)	
Cyanate	—OCN
N-Cyanourea	—NHCONHCN

^a Data from Harris and Spinelli,²⁴ Hergenrother,²⁵ Harris et al.,²⁶ Droske and Stille,²⁷ Stille and Droske,²⁸ Keszler et al.,²⁹ Delos et al.,³⁰ Stenzenberger et al.,³¹ and Varma et al.³²

have a planar zig-zag conformation like PE, are highly crystalline, and the T_m is raised by:

(i) The number of amide groups per $-\text{CH}_2-$ group. Thus:

Nylon: Nylon 4 Nylon 6 Nylon 7 Nylon 11 Nylon 12
 T_m : 262°C 215°C 235°C 194°C 179°C
 (cf. T_m for linear PE = 137°C).

(iii) If there is a good fit for hydrogen bonding (Figure 4.26).

Nylon 4,6 has a perfect fit and has been recently introduced as a new engineering nylon by Dutch State Mines (DSM).

(e) The stiffer the main central chain, the less likely the polymer is to crystallise by twisting and folding into the necessary conformation. Table 4.9 shows that many of the aromatic-backbone polymers are amorphous. Fortunately, many of these materials have T_g values above 200°C, giving high heat distortion temperatures (HDTs) (see Figure 4.19).

It could be argued that a high T_g and T_m are good because the HDT will be higher. However, it must be remembered that the polymer must be fabricated, and a rough temperature guide for a suitable melt viscosity for processing is $T_g + 150^\circ\text{C}$ or $T_m + 50^\circ\text{C}$. If T_g and T_m are too high, then the polymer may decompose during fabrication.

Figure 4.26 Hydrogen bonding in various nylons.

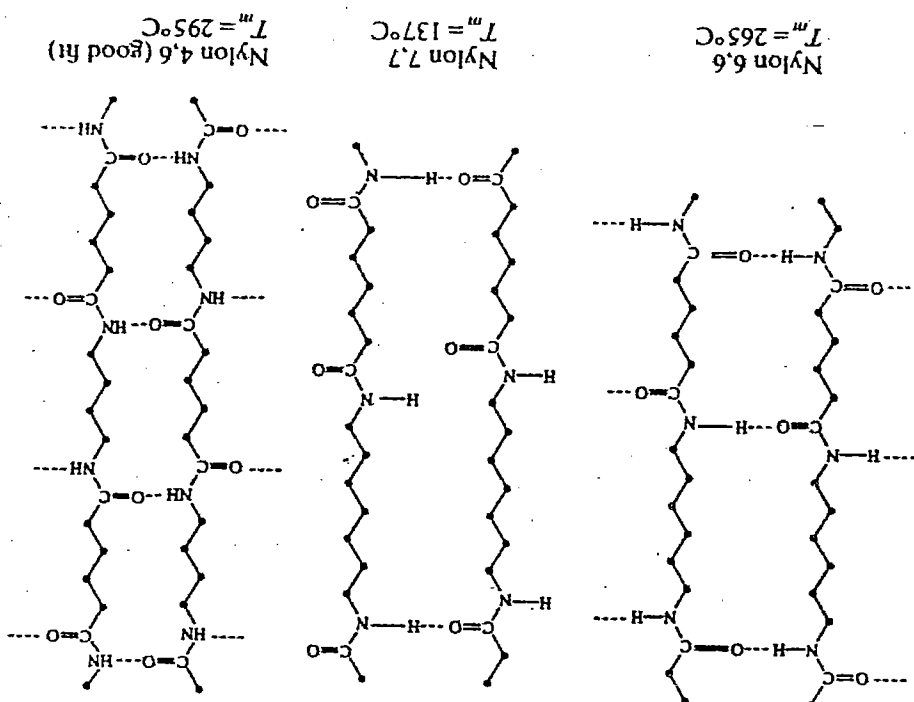


TABLE 6.9. Representative Free Radical Monomer (M) Reactivity Ratios (r)^a

M_1	M_2	r_1	r_2	Temperature (°C)
Styrene	Methyl methacrylate	0.52	0.46	60
Styrene	Acrylonitrile	0.40	0.04	60
Styrene	Vinyl acetate	55	0.01	60
Styrene	Maleic anhydride	0.041	0.01	60
Styrene	Vinyl chloride	17	0.02	60
Styrene	1,3-Butadiene	0.58	1.35	50
Styrene	Isoprene	0.54	1.92	80
Methyl methacrylate	Vinyl chloride	10	0.1	68
Methyl methacrylate	Vinyl acetate	20	0.015	60
Methyl methacrylate	Acrylonitrile	1.20	0.15	60
Methyl methacrylate	1,3-Butadiene	0.25	0.75	90
Ethylene	Tetrafluoroethylene	0.38	0.1	25
Ethylene	Acrylonitrile	0	7	20
Ethylene	Vinyl acetate	0.97	1.02	130

^aData selected from Young^{29a} (see this reference for polymerization conditions).

Clearly, a knowledge of reactivity ratios is of immense benefit in formulating feed ratios for copolymers. Let us examine several hypothetical situations involving different values of r_1 and r_2 . First we consider the situation where

$$r_1 = r_2 = 1.0$$

In this case the monomers would exhibit no preference for homopolymerization or copolymerization, and a truly random copolymer would result. Under these conditions the copolymer equation reduces to

$$F_1 = f_1$$

and a plot of f_1 versus F_1 (Figure 6.1) would show the same composition in both feed and copolymer. A situation approaching this is the copolymerization of ethylene (M_1) and vinyl acetate (M_2) ($r_1 = 0.97$, $r_2 = 1.02$). This is shown by curve A in Figure 6.1, which is very close to the diagonal.

Next we consider the case where

$$r_1 = r_2 = 0$$

Here, neither monomer would exhibit a tendency to homopolymerize, and a truly alternating copolymer would result. Then $F_1 = 0.5$. Approaching this situation is the styrene (M_1)-maleic anhydride (M_2) system where $r_1 = 0.041$ and $r_2 = 0.01$. This is shown by curve B in Figure 6.1.

A far more common situation is where both r_1 and r_2 lie between 0 and 1, such as with the styrene (M_1)-methyl methacrylate (M_2) system ($r_1 = 0.52$, $r_2 = 0.46$), shown by curve C in Figure 6.1. In such cases there is some tendency toward alternation. (If $r_1 = 0.5$, M_1 reacts twice as fast with M_2 as with M_1 .) The point at which curve C crosses the diagonal represents a composition where polymerization proceeds to relatively high conversion with no

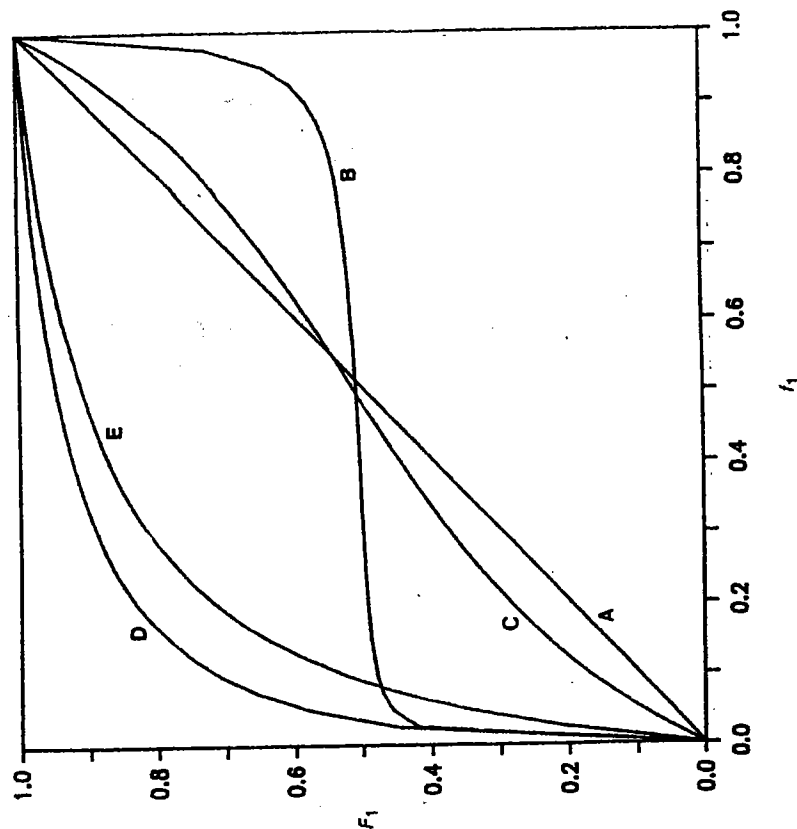


FIGURE 6.1. Variation of F_1 , f_1 , and r in copolymerization (F_1 = mole fraction of monomer in copolymer; f_1 = mole fraction of monomer in feed; r = reactivity ratio): (A) $r_1 = 0.97$, $r_2 = 1.02$; (B) $r_1 = 0.041$, $r_2 = 0.01$; (C) $r_1 = 0.52$, $r_2 = 0.46$; (D) $r_1 = 55$, $r_2 = 0.01$; (E) $r_1 = 10$, $r_2 = 0.1$.

change in either feed ratio or copolymer composition. Such cases are called *azeotropic polymerization*. Since with azeotropic polymerization

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]}$$

the copolymer equation reduces to

$$\frac{[M_1]}{[M_2]} = \frac{1 - r_2}{1 - r_1}$$

under azeotropic conditions. Azeotropic polymerization is also possible, in principle, when both r_1 and r_2 are greater than 1; however, this situation has not been observed in free radical copolymerization.

Table 7.3. Representative cationic reactivity ratios, (*r*)^a

Monomer 1	Monomer 2	Co-initiator ^b	Solvent ^c	Temperature (°C)	<i>r</i> ₁	<i>r</i> ₂
Isobutylene	1,3-Butadiene	AlEtCl ₂	CH ₃ Cl	-100	43	0
	1,3-Butadiene	AlCl ₃	CH ₃ Cl	-103	115	0
	Isoprene	AlCl ₃	CH ₃ Cl	-103	2.5	0.4
	Cyclopentadiene	BF ₃ ·OEt ₂	φCH ₃	-78	0.60	4.5
	Styrene	SnCl ₄	EtCl	0	1.60	0.17
	Styrene	AlCl ₃	CH ₃ Cl	-92	9.02	1.99
	α-Methylstyrene	TiCl ₄	φCH ₃	-78	1.2	5.5
	α-Methylstyrene	SnCl ₄	EtCl	0	0.05	2.90
Styrene	α-Methylstyrene	SnCl ₄	CCl ₄	-78	0.33	1.74
	<i>p</i> -Methylstyrene	SnCl ₄	CH ₂ Cl ₂	0	1.80	0.10
	<i>trans</i> -β-Methylstyrene	SnCl ₄	CH ₂ Cl ₂	0	1.0	0.32
<i>p</i> -Chlorostyrene	<i>cis</i> -β-Methylstyrene	SnCl ₄	CCl ₄ /φNO ₂ (1:1)	0	0.74	0.32
	<i>trans</i> -β-Methylstyrene	SnCl ₄	CCl ₄ /φNO ₂ (1:1)	-78	1.30	0.92
Ethyl vinyl ether	<i>t</i> -Butyl vinyl ether	BF ₃	CH ₂ Cl ₂	-23	6.02	0.42
2-Chloroethyl vinyl ether	α-Methylstyrene	BF ₃	CH ₂ Cl ₂			

^a Data from Kennedy and Marechal.¹^b Et = C₂H₅, φ = phenyl.Table 7.5. Representative anionic reactivity ratios (*r*)^a

Monomer 1	Monomer 2	Initiator ^b	Solvent ^c	Temperature (°C)	<i>r</i> ₁	<i>r</i> ₂
Styrene	Methyl methacrylate	Na	NH ₃	d	0.12	6.4
		<i>n</i> -BuLi	None	d	e	e
		<i>n</i> -BuLi	None	25	0.04	11.2
	Butadiene	<i>n</i> -BuLi	Hexane	25	0.03	12.5
		<i>n</i> -BuLi	Hexane	50	0.04	11.8
		<i>n</i> -BuLi	THF	25	4.0	0.3
		<i>n</i> -BuLi	THF	-78	11.0	0.4
		EtNa	Benzene	d	0.96	1.6
		<i>n</i> -BuLi	Cyclohexane	40	0.046	16.6
	Isoprene	RLi	None	d	0.12	12.5
	Acrylonitrile	Na	NH ₃	d	0.01	0.01
	Vinyl acetate	<i>n</i> -BuLi	Hexane	50	3.38	0.47
Butadiene	Isoprene	<i>n</i> -BuLi	Hexane	d	0.25	7.9
	Acrylonitrile	NANH ₂	NH ₃	d	0.34	6.7
Methyl methacrylate		RLi	None	d	3.2	0.4
	Vinyl acetate	NANH ₂	NH ₃	d		

^a Data from Morton.²⁹^b Bu = butyl, Et = ethyl, R = alkyl.^c THF = tetrahydrofuran.

Table 7.3. Representative cationic reactivity ratios, (*r*)^a

Monomer 1	Monomer 2	-Cofinitiator ^b	Solvent ^b	Temperature (°C)	<i>r</i> ₁	<i>r</i> ₂
Isobutylene	1,3-Butadiene	AlEtCl ₂	CH ₂ Cl	-100	43	0
	1,3-Butadiene	AlCl ₃	CH ₂ Cl	-103	115	0
	Isoprene	AlCl ₃	CH ₂ Cl	-103	2.5	0.4
	Cyclopentadiene	BF ₃ ·OEt ₂	φCH ₃	-78	0.60	4.5
	Styrene	SnCl ₄	EtCl	0	1.60	0.17
	Styrene	AlCl ₃	CH ₂ Cl	-92	9.02	1.99
	α-Methylstyrene	TiCl ₄	φCH ₃	-78	1.2	5.5
	α-Methylstyrene	SnCl ₄	EtCl	0	0.05	2.90
	<i>p</i> -Methylstyrene	SnCl ₄	CCl ₄	-78	0.33	1.74
	<i>trans</i> -β-Methylstyrene	SnCl ₄	CH ₂ Cl ₂	0	1.80	0.10
	<i>cis</i> -β-Methylstyrene	SnCl ₄	CCl ₄ /φNO ₂ (1:1)	0	1.0	0.32
	<i>trans</i> -β-Methylstyrene	SnCl ₄	CCl ₄ /φNO ₂ (1:1)	0	0.74	0.32
	<i>i</i> -Butyl vinyl ether	BF ₃	CH ₂ Cl ₂	-78	1.30	0.92
	2-Chloroethyl vinyl ether	BF ₃	CH ₂ Cl ₂	-78	6.02	0.42

^a Data from Kennedy and Marchal.¹^b Et = C₂H₅, φ = phenyl.Table 7.5. Representative anionic reactivity ratios (*r*)^a

Monomer 1	Monomer 2	Initiator ^b	Solvent ^c	Temperature (°C)	<i>r</i> ₁	<i>r</i> ₂
Styrene	Methyl methacrylate	Na	NH ₃	d	0.12	6.4
		<i>n</i> -BuLi	None	d	e	e
	Butadiene	<i>n</i> -BuLi	None	25	0.04	11.2
		<i>n</i> -BuLi	Hexane	25	0.03	12.5
		<i>n</i> -BuLi	Hexane	50	0.04	11.8
		<i>n</i> -BuLi	THF	25	4.0	0.3
		<i>n</i> -BuLi	THF	-78	11.0	0.4
		EtNa	Benzene	d	0.96	1.6
	Isoprene	<i>n</i> -BuLi	Cyclohexane	40	0.046	16.6
		RLi	None	d	0.12	12.5
	Acrylonitrile	RLi	None	d	0.01	0.01
	Vinyl acetate	Na	NH ₃	d	0.01	0.47
Butadiene	Isoprene	<i>n</i> -BuLi	Hexane	50	3.38	7.9
	Acrylonitrile	NANH ₂	NH ₃	d	0.25	6.7
		RLi	None	d	0.34	3.2
Methyl methacrylate	Vinyl acetate	NANH ₂	NH ₃	d	0.4	0.4

^a Data from Morton.²⁹^b Bu = butyl, Et = ethyl, R = alkyl.^c THF = tetrahydrofuran.

Table 7.3. Representative cationic reactivity ratios, (*r*)^a

Monomer 1	Monomer 2	Co-initiator ^b	Solvent ^b	Temperature (°C)	<i>r</i> ₁	<i>r</i> ₂
Isobutylene	1,3-Butadiene	AlEtCl ₂	CH ₃ Cl	-100	43	0
	1,3-Butadiene	AlCl ₃	CH ₃ Cl	-103	115	0
	Isoprene	AlCl ₃	CH ₃ Cl	-103	2.5	0.4
	Cyclopentadiene	BF ₃ ·OEt ₂	φCH ₃	-78	0.60	4.5
	Styrene	SnCl ₄	EtCl	0	1.60	0.17
	Styrene	AlCl ₃	CH ₃ Cl	-92	9.02	1.99
	Styrene	TiCl ₄	φCH ₃	-78	1.2	5.5
Styrene	<i>a</i> -Methylstyrene	SnCl ₄	EtCl	0	0.05	2.90
	<i>p</i> -Methylstyrene	SnCl ₄	CCl ₄	-78	0.33	1.74
	<i>trans</i> -β-Methylstyrene	SnCl ₄	CH ₂ Cl ₂	0	1.80	0.10
	<i>cis</i> -β-Methylstyrene	SnCl ₄	CCl ₄ /φNO ₂ (1:1)	0	1.0	0.32
	<i>trans</i> -β-Methylstyrene	SnCl ₄	CCl ₄ /φNO ₂ (1:1)	0	0.74	0.32
Ethyl vinyl ether	<i>t</i> -Butyl vinyl ether	BF ₃	CH ₂ Cl ₂	-78	1.30	0.92
2-Chloroethyl vinyl ether	<i>a</i> -Methylstyrene	BF ₃	CH ₂ Cl ₂	-23	6.02	0.42

^a Data from Kennedy and Marechal.¹^b Et = C₂H₅, φ = phenyl.Table 7.5. Representative anionic reactivity ratios (*r*)^a

Monomer 1	Monomer 2	Initiator ^b	Solvent ^c	Temperature (°C)	<i>r</i> ₁	<i>r</i> ₂
Styrene	Methyl methacrylate	Na	NH ₃	d	0.12	6.4
		<i>n</i> -BuLi	None	d	e	e
	Butadiene	<i>n</i> -BuLi	None	25	0.04	11.2
		<i>n</i> -BuLi	Hexane	25	0.03	12.5
		<i>n</i> -BuLi	Hexane	50	0.04	11.8
		<i>n</i> -BuLi	THF	25	4.0	0.3
		<i>n</i> -BuLi	THF	-78	11.0	0.4
		EtNa	Benzene	d	0.96	1.6
	Isoprene	<i>n</i> -BuLi	Cyclohexane	40	0.046	16.6
	Acrylonitrile	RLi	None	d	0.12	12.5
	Vinyl acetate	Na	NH ₃	d	0.01	0.01
Butadiene	Isoprene	<i>n</i> -BuLi	Hexane	50	3.38	0.47
Methyl methacrylate	Acrylonitrile	NaNH ₂	NH ₃	d	0.25	7.9
		RLi	None	d	0.34	6.7
	Vinyl acetate	NaNH ₂	NH ₃	d	3.2	0.4

^a Data from Morton.²⁹^b Bu = butyl, Et = ethyl, R = alkyl.^c THF = tetrahydrofuran.^d Temperature not specified.^e No detectable styrene in polymer.

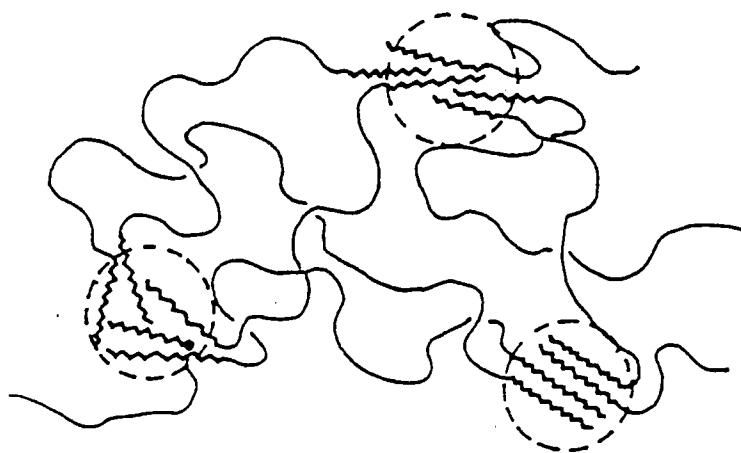


FIGURE 3.20. Representation of aggregation in an ABA block thermoplastic elastomer (— represents end blocks, circle represents microdomains).

of the mechanical and solution properties of crystalline polymers resemble those of crosslinked amorphous polymers. Certain materials intermolecularly associated through hydrogen bonds also behave like crosslinked polymers. Gelatin, an animal-derived protein that

TABLE 3.6. Commercially Important Thermoplastic Elastomers

Type	End Blocks	Middle Block
Styrenic	Polystyrene	Polybutadiene or polyisoprene
Polyolefin ^a	Isotactic polypropylene	Ethylene-propylene copolymer
Polyurethane	Rigid polyurethane	Flexible polyester or polyether
Copolyester	Rigid polyester ^b	Flexible polyester
Polyamide	Rigid polyamide ^c	Flexible polyether

^aAlso manufactured by mechanical blending of isotactic polypropylene and ethylene-propylene-diene copolymer.

^bPrincipally poly(ethylene terephthalate).

^cNylons 6, 66, 11, 12, and 612.

however, there has been a resurgence of interest arising primarily from the demand for engineering plastics and specialty elastomers and fibers. There are sound economic reasons for this interest. Development of a new polymer to meet a specific need is a costly enterprise. If the desired properties can be realized simply by mixing two or more existing polymers, there is an obvious pecuniary advantage.

TABLE 3.7. Types of Polyblends

Type	Description
Mechanical blends	Polymers are mixed at temperatures above T_g or T_m for amorphous and semicrystalline polymers, respectively
Mechanochemical blends	Polymers are mixed at shear rates high enough to cause degradation. Resultant free radicals combine to form complex mixtures including block and graft components
Solution-cast blends	Polymers are dissolved in common solvent and solvent is removed
Latex blends	Fine dispersions of polymers in water (latexes) are mixed, and the mixed polymers are coagulated
Chemical blends	Crosslinked polymer is swollen with different monomer, then monomer is polymerized and crosslinked
Interpenetrating polymer networks (IPN)	Polyfunctional monomer is mixed with thermoplastic polymer, then monomer is polymerized to network polymer (also called pseudo-IPN)
Semi-interpenetrating polymer networks (semi-IPN)	Different monomers are mixed, then homopolymerized and crosslinked simultaneously, but by noninteracting mechanisms
Simultaneous interpenetrating polymer networks (SIN)	Latex polyblend is crosslinked after coagulation
Interpenetrating elastomeric networks (IEN)	

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Table 1.5. Principal engineering plastics

Type	Abbreviation	Chapter where discussed
Acetal ^a	POM	11
Polyamide ^b	—	13
Poly(amideimide)	PAI	13
Polyarylate	—	12
Polycarbonate	PC	12
Polyester ^c	—	12
Polyetheretherketone	PEEK	11
Polyetherimide	PEI	11
Polyimide	PI	13
Poly(phenylene oxide)	PPO	11
Poly(phenylene sulfide)	PPS	11
Polysulfone ^d	—	11

^a Common name for polyformaldehyde. Abbreviation refers to poly(oxymethylene).

^b Principally nylons 6 and 66.

^c Principally poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT).

^d Marketed.

Table 1.6. Principal thermosetting plastics

Type	Abv.	Typical uses	Chapter where discussed
Phenol-formaldehyde	PF	Electrical and electronic equipment, automobile parts, utensil handles, plywood adhesives, particle board binder	14
Urea-formaldehyde	UF	Similar to PF polymers; also treatment of textiles, coatings	14
Unsaturated polyester	—	Construction, automobile parts, boat hulls, marine accessories, corrosion-resistant ducting, pipe, tanks, etc., business equipment	12
Epoxy	—	Protective coatings, adhesives, electrical and electronics applications, industrial flooring, highway paving materials, composites	11
Melamine-formaldehyde	MF	Similar to UF polymers; decorative panels, counter and table tops, dinnerware	14

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Table 1.7. Principal synthetic fibers

Type	Description
Cellulosic	—
Acetate rayon	Cellulose acetate
Viscose rayon	Regenerated cellulose
Noncellulosic	—
Polyester	Principally poly(ethylene terephthalate)
Nylon	Includes nylon 66, nylon 6, and variety of other aliphatic and aromatic polyamides
Olefin	Includes polypropylene and copolymers of vinyl chloride, with lesser amounts of acrylonitrile, vinyl acetate, or vinylidene chloride ($\text{CH}_2 = \text{CCl}_2$) (copolymers consisting of more than 85% vinyl chloride are called <i>vinylon</i> fibers)
Acrylic	Contain at least 80% acrylonitrile; included are <i>modacrylic</i> fibers comprising acrylonitrile and about 20% vinyl chloride or vinylidene chloride

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Table 1.8. Principal types of synthetic rubber

Type	Description
Styrene-butadiene	Copolymer of the two monomers in various proportions depending on properties desired; called SBR for styrene-butadiene rubber
Polybutadiene	Consists almost entirely of the <i>cis</i> -1,4 polymer
Ethylene-propylene	Often abbreviated EPDM for ethylene-propylene-diene monomer; made up principally of ethylene and propylene units with small amounts of a diene to provide unsaturation
Polychloroprene	Principally the <i>trans</i> -1,4 polymer, but also some <i>cis</i> -1,4 and 1,2 polymer; also known as <i>neoprene</i> rubber
Polyisoprene	Mainly the <i>cis</i> -1,4 polymer; sometimes called "synthetic natural rubber"
Nitrile	Copolymer of acrylonitrile and butadiene, mainly the latter
Butyl	Copolymer of isobutylene and isoprene, with only small amounts of latter
Silicone	Contains inorganic backbone of alternating oxygen and methylated silicon atoms; also called polysiloxane (Chap. 15)
Urethane	Elastomers prepared by linking polyethers through urethane groups (Chap. 13)

Table 4.6. Polymer additives

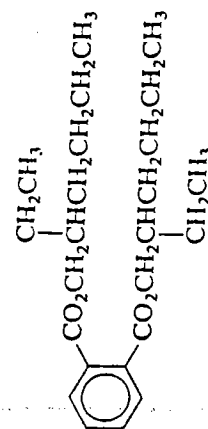
Type	Function
Mechanical property modifiers	
Plasticizers	Increase flexibility
Impact modifiers	Improve impact strength
Reinforcing fillers	Increase strength properties
Nucleating agents	Modify crystalline morphology
Surface property modifiers	
Slip and antiblocking agents	Prevent film and sheet sticking
Lubricants	Prevent sticking to machinery
Antistatic agents	Prevent static charge on surfaces
Coupling agents	Improve bonding between polymer and filler
Wetting agents	Stabilize dispersions of filler
Antifogging agents	Disperse moisture droplets on films
Chemical property modifiers	
Flame retardants	Reduce flammability
Ultraviolet stabilizers	Improve light stability
Antioxidants	Prevent oxidative degradation
Biocides	Prevent mildew
Aesthetic property modifiers	
Dyes and pigments	Impart color
Odorants	Add fragrance
Deodorants	Prevent development of odor
Nucleating agents	Improve light transmission
Processing modifiers	
Plasticizers	Reduce melt viscosity
Slip agents and lubricants	Prevent sticking to processing machinery
Low-profile additives	Prevent shrinkage and warpage
Thickening agents	Increase viscosity of polymer solutions or dispersions
Heat stabilizers	Prevent degradation during processing
Defoaming agents	Reduce foaming
Blowing agents	Manufacture stable foams
Emulsifiers	Stabilize polymer emulsions
Crosslinking (curing) agents	Crosslink polymer
Promoters	Speed up crosslinking (curing)

در این بخش به بررسی انواع افزودنی‌های پلیمری و کاربردهای آنها پرداخته می‌شود. این افزودنی‌ها می‌توانند خواص فیزیکی و شیمیایی پلیمر را تغییر دهند و به بهبود عملکرد آن در شرایط مختلف کمک کنند.

Table 4.7. Commonly used plasticizers

Aromatic	
Di-2-ethylhexyl phthalate	
Di-n-octyl phthalate	
Di-4-octyl phthalate	
Di-4-decyl phthalate	
Di-n-undecyl phthalate	
Di-n-tridecyl phthalate	
Tri-2-ethylhexyl trimellitate	
Aliphatic	
Di-2-ethylhexyl adipate	
Di-2-ethylhexyl sebacate	
Di-2-ethylhexyl azelate	
Epoxy	
Epoxidized linseed oil	
Epoxidized soya oil	
Polyneric	
Poly(alkylene adipates, sebacates, or azelates)	
Fire retardant	
Chlorinated paraffins	
Phosphate esters	

thermal motion of the low-molecular-weight plasticizers increases the polymer's free volume, allowing more "elbow/room" for increased long-range segmental motion of the polymer molecules. For some applications, plasticizer comprises almost 50% of the formulation and, in the case of poly(vinyl chloride), the glass transition temperature may be reduced from about 80°C for unplasticized polymer to below 0°C. For reasons of compatibility, plasticizers are not used with highly crystalline polymers.



A number of criteria are considered in choosing a plasticizer, including cost, compatibility, stability, processability, and permanence. Permanence refers to how well the plasticizer remains in the polymer: Will it vaporize on heating or be extracted if the plastic comes into contact with solvents or

TABLE 12.1 Types of fillers for polymers

Organic materials	
A. Cellulosic products	1. Wood products
	a. Kraft paper
	b. Chips
	c. Coarse flour
	d. Ground flour
	(1) Softwood flour
	(2) Hardwood flour
	(3) Shell flour
2. Communitized cellulose products	a. Chopped paper
	b. Diced resin board
	c. Crepe paper
	d. Pulp preforms
3. Fibers	a. α -Cellulose
	b. Pulp preforms
	c. Cotton flock
	d. Textile byproducts
B. Lignin-type products	g. Rayon
	1. Ground bark
	2. Processed lignin
C. Synthetic fibers	1. Polyamides (nylon)
	2. Polyesters (Dacron)
	3. Polyacrylonitrile (Orlon, Acrilan)
D. Carbon	1. Carbon black
	a. Channel black
	b. Furnace black
	2. Ground petroleum coke
	3. Graphite filaments
	4. Graphite whiskers
Inorganic materials	
A. Silica products	1. Minerals
	a. Sand
	b. Quartz
	c. Tripoli
	d. Diatomaceous earth
2. Synthetic materials	a. Wet-processed silica
	b. Pyrogenic silica
	c. Silica aerogel
B. Silicates	a. Minerals
	(1) Clayminerals
	(2) Amorphous
C. Glass	
	1. Glass flakes
	2. Solid glass spheres
	3. Hollow glass spheres
	4. Milled fibers
	5. Fibrous glass
	a. Filament
	b. Rovings
	c. Woven roving
	d. Yarn
	e. Mat
	f. Fabric
D. Metals	
E. Boron filaments	
F. Metallic oxides	1. Ground material
	a. Zinc oxide
	b. Alumina
	c. Magnesia
	d. Titania
	2. Whiskers
	a. Aluminum oxide (sapphire)
	b. Beryllium oxide
	c. Magnesium oxide
	d. Thorium oxide
	e. Zirconium oxide
C. Calcium carbonate	1. Chalk
	2. Limestone
	3. Precipitated calcium carbonate
H. Polytetrafluorocarbons	
I. Other fillers	1. Whiskers (nonoxide)
	a. Aluminum nitride
	b. Beryllium carbide
	c. Boron carbide
	d. Silicon carbide
	e. Silicon nitride
	f. Tungsten carbide
	2. Barium ferrite
	3. Barium sulfate

12.2 Fillers

Silica, which has a specific ring and synthetic amorphous tailing particulates such as s. Diatomaceous earth, also Fuller's earth, is a finely divided tons of diatoms. This filler is used to prevent rolls of film from increasing the compressive strength stone, is porous silica for pyrogenic, or fumed, silica. ing silicon tetrachloride in an filler is used as a thixotropic. Finely divided silicas are also care solutions and by the evaporation. Sharp silica sand is used Reactive silica ash produced novaculite, from the novaculite fillers in polymers. Hydrated finely divided silicas are used for the reinforcement in handling silica to prevent silicas fillers are used annually. Both naturally occurring as fillers. Hydrated aluminum of 2.6 and a hardness value of silicas may be dissolved in sodium silicate. Clays are bituminous products. Mica, which has a specific ratio below 30. However, mosaic delamination. Talc is a naturally occurring with a Mohs' hardness of 1 a polypropylene is much more motive accessories subject to talc are used annually as fillers. Nepheline syenite, a natural silicate filler, and wollastonite are used for the reinforcement or slag (PMI) are also used. Asbestos is a naturally of its toxicity has been used approximately 180 million lb for polymers.

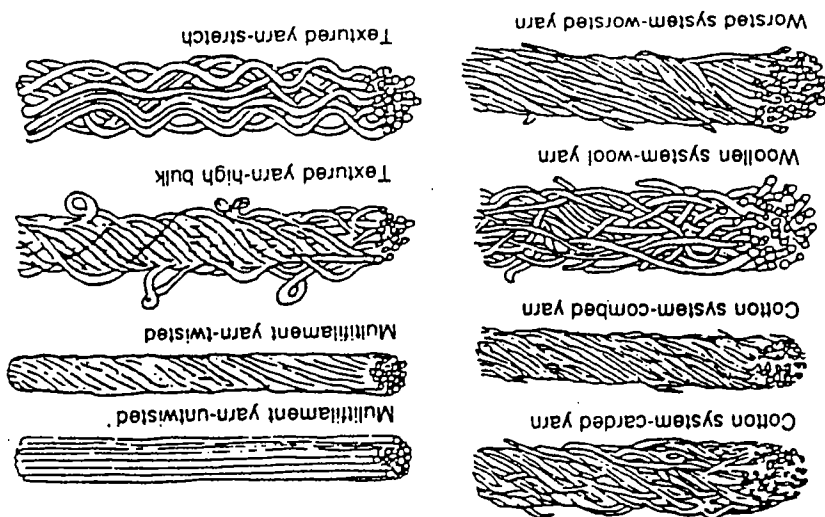


Figure 4.13 Schematic description of spun and multifilament yarns.

Requirements to be met by textile fibres	
Properties of the final product	Corresponding fibre properties
Optical properties	Lustre, fibre surface
Aesthetics	Profile, fibre cross section
Mechanical properties	Modulus of elasticity, tenacity, elongation
Comfort	Moisture absorption, moisture transport
Physiological properties of clothing	Electrical resistance
Antistatics	Heat capacity, porosity, heat conduction
Hand	Textile structure, bending modulus
Feel	Roughness, modulus of elasticity, fineness
Ease of care and washability	Wetting, moisture absorption, glass transition point (wet)
Dry cleaning	Polymer (in)solubility, swelling
Soiling characteristics	Zeta potential, adsorption and dissolution of soil components
Fastness	Tenacity, elongation, moduli, abrasion resistance
Mechanical stability	Melting point, glass transition point (wet and dry)
Dimensional stability	Thermoplasticity, glass transition temperature (T_g)
Forming (e.g. pleating)	Chemical structure, sensitisers, stabilisers
Lighfastness	Polymer-dye interaction, radical lifetime
Lighfastness of dyeing	Chemical structure, combustion mechanism
Specific properties	Moisture absorption, wetting properties
Flame resistance	Surface properties, morphology, yarn structure
Impermeability to water	Glass transition point during dyeing
Water vapour permeability	Modulus of elasticity, tenacity, elongation, dynamic modulus
Dyeability	Chemical structure, glass transition temperature, morphological structure, domain structure
Mechanical properties (ropes, material, tyre cord)	
Rubber elasticity	

horizontal section is where the 'tie' molecules between the lamellae are being orientated; this is non-reversible.

The extent of draw affects the tenacity of the fibre; in fibres for apparel (i.e. soft and flexible) a low draw is used, whereas fibres with high strength (e.g. nylon for tyre cords) require a high draw ratio. Originally this led to irreversible changes in finished garments (e.g. baggy trousers, kneed stockings), but advances in knitting technology and elastomeric fibres have eliminated this. For dimensional stability for water washing, PET fibres, after drawing, are given a steam treatment for ~5 min.

With amorphous fibres such as PAN, well-defined crystalline lamellae are not formed (strong dipole-dipole interaction occurs), but the act of drawing still increases the strength.

The drawing of fibres should, in principle, be above T_g , or else brittle fracture may occur. Thus PET and PAN fibres are heated during drawing. In some cases, especially when solution spinning is used, the residual solvent lowers T_g . A similar situation occurs with nylon at high humidity or containing low-MW impurities.

4.9.3 Mechanical strength of fibres

The diameter of monofilament fibres is in the range 10–50 μm , but is variable and non-uniform (i.e. not always circular). Therefore the mechanical strength of fibres is quoted against the weight of a length of fibre (i.e. force per unit linear density):

$$1 \text{ tex} = 1 \text{ g per } 1000 \text{ m of fibre}$$

thus if 1000 m = 1 g, then the fineness is 1 tex; if 1000 m = x g, then the fineness is x tex. The higher the tex, the coarser the fibre. Originally the definition was 1 denier = 1 g per 9000 m of fibre, and in order to keep the tex term similar, dtex (mass per 10000 m) is often used.

Thus the mechanical properties are based upon weight rather than area (e.g. $1 \text{ N/m}^2 = 1 \text{ Pa}$ or $1 \text{ N/mm}^2 = 1 \text{ MPa}$). Thus, maximum tensile force (at break)—called tenacity—is expressed in N/tex (or N/dtex , cN/tex , etc.), where

Table 4.14 Requirements to be met by textile fibres

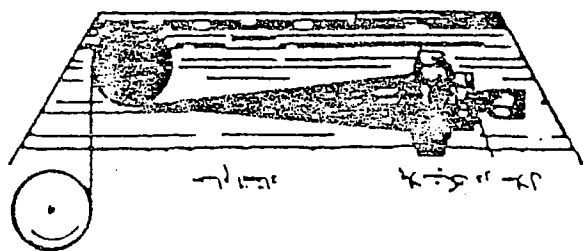
Properties of the final product	Corresponding fibre properties
Optical properties	Lustre, fibre surface
Aesthetics	Profile, fibre cross section
Mechanical properties	Modulus of elasticity, tenacity, elongation
Comfort	Moisture absorption, moisture transport
Physiological properties of clothing	Electrical resistance
Antistatics	Heat capacity, porosity, heat conduction
Thermal insulation	Textile structure, bending modulus
Hand	Roughness, modulus of elasticity, fineness
Feel	Wetting, moisture absorption, glass transition point (wet)
Ease of care and washability	Polymer (insolubility, swelling
Dry cleaning	Zeta potential, adsorption and dissolution of soil components
Soiling characteristics	Tenacity, elongation, moduli, abrasion resistance
Fastness	Melting point, glass transition point (wet and dry)
Mechanical stability	Thermoplasticity, glass transition temperature (T_g)
Dimensional stability	Chemical structure, sensitisers, stabilisers
Forming (e.g. pleating)	Polymer-dye interaction, radical lifetime
Lightfastness	
Lightfastness of dyeing	
Specific properties	
Flame resistance	Chemical structure, combustion mechanism
Impermeability to water	Moisture absorption, wetting properties
Water vapour permeability	Surface properties, morphology, yarn structure
Dyeability	Glass transition point during dyeing
Mechanical properties (ropes, material, tyre cord)	Modulus of elasticity, tenacity, elongation, dynamic modulus
Rubber elasticity	Chemical structure, glass transition temperature, morphological structure, domain structure

the textile is constructed, i.e. how the monofilaments are put together (Figure 4.43), and also whether the finished textile article is woven or knitted.

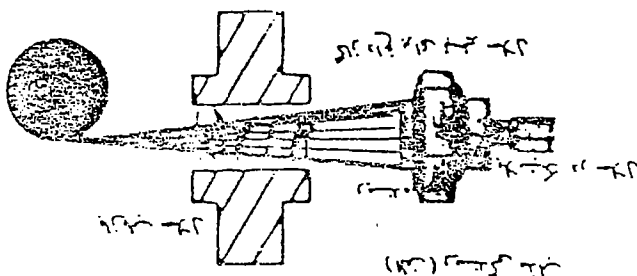
Staple fibres, being of short length (3–12 cm) and not continuous, are twisted together to form a continuous yarn, like wool and cotton.

For apparel fibres, the effect of temperature on the textile is important. Not only has the T_g of the fibre to be low enough to permit ironing, but the T_g must

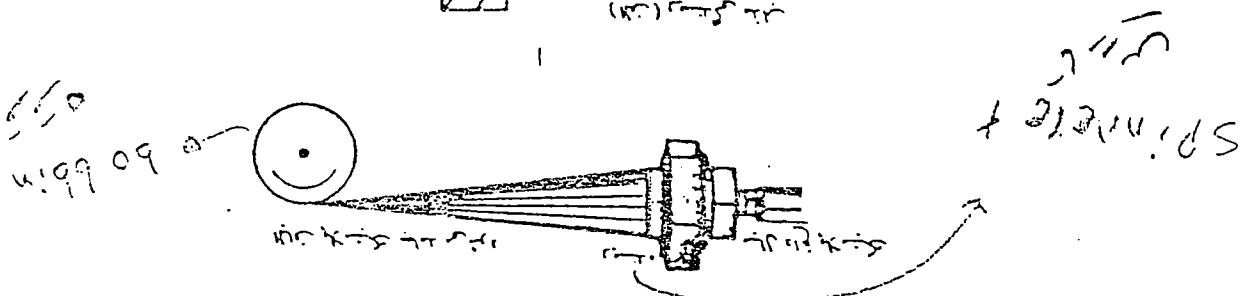
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شکل ۸-۱۲. سنج راکول.

سنگه بر بزرگتر خواهد بود

برای سنجش راکول در متریال آن را سنجش بر روی

سنگه

به نقطه R بار

است. بر روی

چیزی بر بزرگتر

می شود ولی بار

بار صاف برداشته

سنگه قرار دهید.

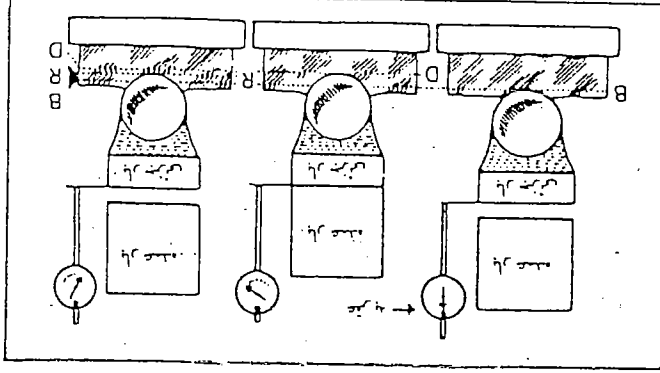
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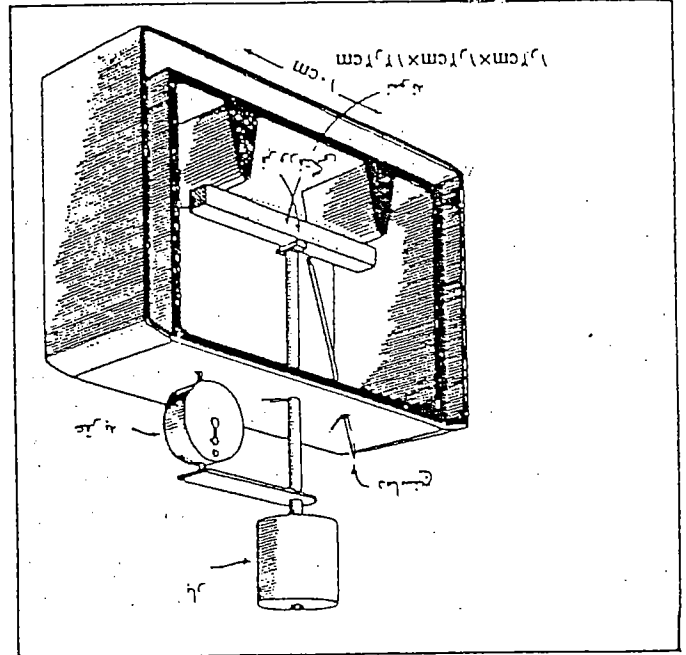
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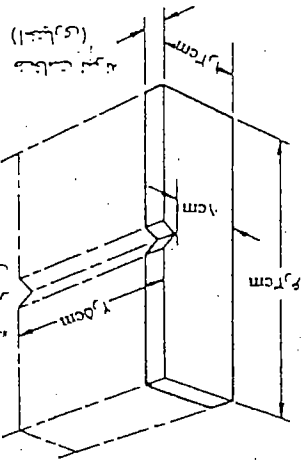
بار چیزی و کلی به



شکل ۸-۱۱. آزمون سنجش راکول.



شکل ۸-۱۳. سنج راکول.



۲۵ سانتی متر

بر اساس ۲۵ سانتی متر

مقدار خرد به سطح بند

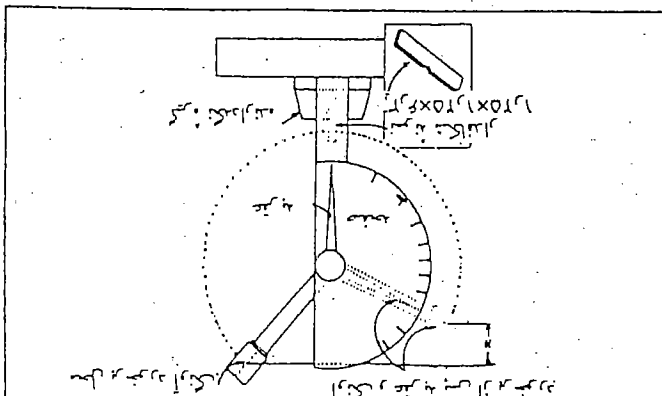
۲۵ سانتی متر

۲۵ سانتی متر

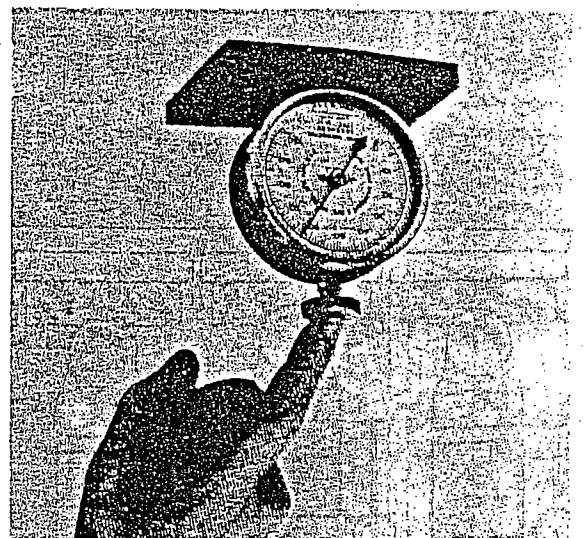
۲۵ سانتی متر

۲۵ سانتی متر

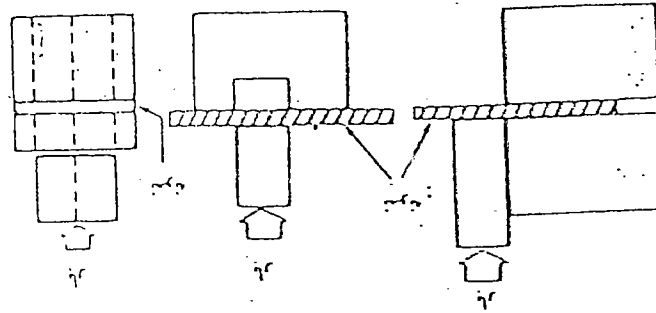
شکل ۸-۱۴. سنج راکول.



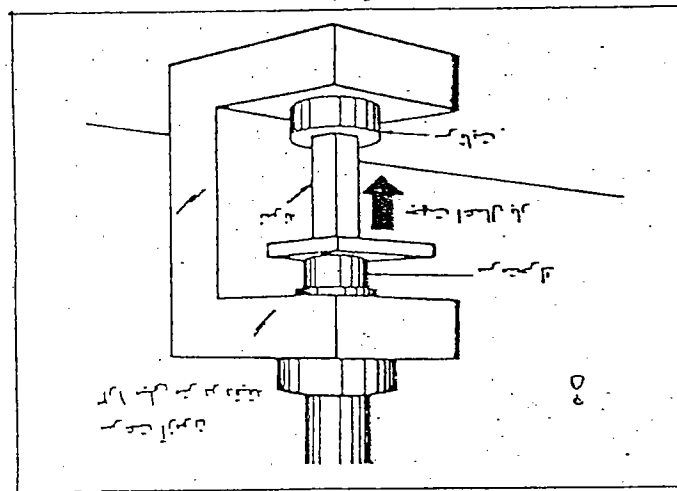
شکل ۸-۱۵. سنج راکول.



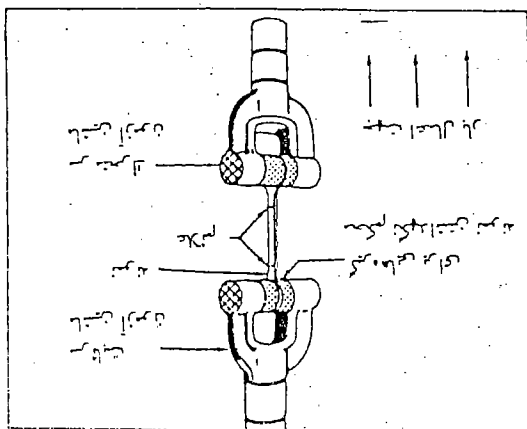
نشان دهنده روش های گوناگون مورد استفاده برای آزمون استحکام برشی پلاستیکی با شکل ۱۰ - روش های گوناگون مورد استفاده برای آزمون استحکام برشی پلاستیکی



شکل ۱۲-۵. دستگاه آزمايش تراكم



شکل ۱۲-۲. دستگاه سنجش کشش پلاستيکي



شکل ۱۲-۳. دستگاه سنجش خم پلاستيکي

