Chapter 2

Experimental Aspects

2.1 Purity Requirements : General Introduction[5]

The purpose of this purification section is to describe, by class, the various materials used in typical polymer syntheses and their various roles in the reactions. Particular emphasis is placed on the requirements for their purity and the means by which these requirements are met, since chemical purity and freedom from interfering contaminants is of special importance if one is to produce polymers of high molecular weight in good yield.

The purity of commercially available monomers is usually not high enough for their use, without treatment, in well-controlled polymerization reactions. Even 10^{-2} -10^{-4} % impurity can have a significant effect on polymerization kinetics. Anionic polymerizations are especially susceptible to impurities at even lower concentrations than these. Consequently, monomers must be stored with care, usually in sealed tubes under an inert atmosphere, and kept at low temperatures in the dark. Even the closured for flasks or containers should be selected for their inertness ; aluminium foil and polytetrafluoroethylene being good examples of inert materials.

Common impurities in monomers may originate (a) during their production (for example, ethyl benzene or divinyl benzene in styrene), (b) as a result of oxidation (peroxides in dienes, benzaldehyde in styrene), (c) from handling and storage (depending on the materials from which the containers are made), (d) or from partial polymerization to oligomers.

In stepwise polymerization, the presence of monofunctional reactions, which can use up functional groups and destroy the stoichiometric equivalent, must be avoided. In addition polymerization, however, it is especially important to avoid water and compounds containing hydroxyl or carbonyl groups ; these can be tolerated only in amounts of less than about 0.05% by weight in most cases.

Although each monomer and polymerization method has its own special requirements, some generally useful purification procedures include simple distillation or distillation under an enert atmosphere, recrystallization, and chromatography. A typical laboratory distillation set up should have a column with height equivalent of 20-30 theoritical plates, a cold trap to protect the vacuum pump, a monostat to maintain the pressure desired (usually 100 torr or less), and a means for introducing inert gas though a thin capillary into the distilland ; this prevents bump-boiling and puges out oxygen.

Some more specific purification routines include the following : for example, water is removed from hydrocarbon monomers by treatment with activated alumina, metal hydrides or oxides, or alkalin metals, such as sodium. Tables 2.1 to 2.4 give useful properties of these and other commomly used drying agents. Olifin impurities, on the other hand, are eliminated by washing the monomer with 36N sulfuric acid whilst aromatic impurities are removed by use of a nitrating mixture. To eliminate impurities containing carbonyl or hydroxyl groups, the monomer can be passed through columns containing activated alumina, molecular sieves, or silica gel. For olefin monomers, the recommended purification method is distillation from reducing agents such as metal hydrides or aluminium alkyls.

Monomers, such as styrene, which undergo sponteneous, if slow, free radical polymerization on storage at room temperature, usually contain small amounts of inhibitors (radical scarengers) when supplied. These can be removed by washing the monomer with dilute acid or base, depending on the type of inhibitor. For example, phenolic inhibitors such as hydroquinone are usually removed with dilute sodium hydroxide. Drying prior to distillation is then carried out with the use of anhydrous salts (Table 2.2).

Finally, monomer of high purity can often be obtained by distilling monomer which has been partially polymerized, say to about 10 % conversion ; vinyl acetate is a typical example. The majority of the unwanted impurities are consumed in reactions leading to the polymer and so are, therefore, not carried over into the monomer distillate.

Drying agent	Suitable for drying	Unsuitable for drying
Phosphorus pentoxide	Alkyl halides, hydrocarbons, halogenated hydrocarbons, carbon disulfide.	Bases, ketones, aldehydes or other materials where polymerization may be caused.
Sulfuric acid	Alkyl halides, saturated hydrocarbons, halogenated hydrocarbons.	Bases, ketones, alcohols, aldehydes, phenols, etc.
Calcium chloride	Ether, esters, alkyl halides, aryl halides, etc.	Alcohols, amines, phenols, aldehydes, amides, fatty acids.

Table 2.1 (Continued)

Drying agent	Suitable for drying	Unsuitable for drying
Potassium hydroxide	Bases	Ketones, aldehydes, esters, acids.
Potassium carbonate	Bases, some halides, ketones	Fatty acids, esters.
Sodium sulfate	Most materials	
magnisium sulfate	most material	
Anhydrous copper sulfate	Ethers, alcohols, etc.	Amines
Sodium	Ethers, saturated hydrocarbons	Alcohols, amines, esters.
Calcium sulfate	Most materials	

Table 2.1 Suitable drying agents for some common classes of organic liquids.

Hydrate	Vapor Pressure, toor	Hydrate	Vapor Pressure, torr
$BaO.H_2O$	10^{-16}	$KOH.H_2O$	1.5
$CaSO_4.\frac{1}{2}H_2O$	0.004	$ZnCl_2.1\frac{1}{2}H_2O$	2.3
$CaCl_2.H_2O$	0.04	$CuSO_4.H_2O$	0.8
$NaOH.H_2O$	0.7	$MgSO_4.H_2O$	1
$CaO.H_2O$	0.8	H_2SO_4, 95 %	0.001
$K_2CO_3.1\frac{1}{2}H_2O$	1.1	$Na_2SO_4.10H_2O$	22.3

Table 2.2 Vapor pressures of hydrates of some common drying agents at 25°C

Drying agent	Gases
CaO	NH_3, amines
$CaCl_2$	H_2, HCl, CO_2, CO, SO_2, N_2, CH_4, O_2, Paraffins, ethers, olefins, alkyl chlorides.
P_2O_5	H_2, O_2, CO_2, CO, SO_2, N_2, CH_4, C_2H_4, paraffins.
H_2SO_4	H_2, N_2, CO_2, Cl_2, CO, CH_4, paraffins.
Fused KOH	NH_3, amines.

Table 2.3 Suitable drying agents for gases.

Reagent	mg/liter gas	% by volume
P_2O_5	2×10^{-15}	-
$Mg(ClO_4)$(anhyd)	5×10^{-4}	-
$Mg(ClO_4)_2 \cdot 3H_2O$(30 % water)	0.002	0.0002
MgO	0.008	0.0007
BaO	0.00065	-
$Ba(ClO_4)_2$(anhyd)	0.82	0.094

Table 2.4 (Continued)

Reagent	mg/liter gas	% by volume
H_2SO_4(95 %)	0.003	0.0003
Alumina	0.003	0.0003
Silica gel (dry)	0.003	0.0003
CaO	0.003	0.0003
$CaCl_2$(granulate)	0.14-0.245	0.0149-0.0264
$CaCl_2$(fused)	0.36	0.0395
$CaSO_4$(anhyd)	0.005	0.005
$CaBr_2$	0.20	0.021
$ZnBr_2$	1.1	0.124
$ZnCl_2$(sticks)	0.8	0.092
$CuSO_4$	1.4	0.165
KOH (fused)	0.014	0.0015
NaOH (fused)	0.16	0.0170

Table 2.4 Equilibrium water-vapor content of gases dried over common reagents at 25°C.

2.2 Purification of Materials used.

The various polymerization materials which are actually used during the cause of this study are categorised in Table 2.5 below:

Monomers	Initiators/Catalyst systems	Solvents
styrene	Benzoyl peroxide	Benzene
Methyl methacrylate	Aluminium trichloride	n-heptane
Acrylonitrile	Lithium metal n-butyl Lithium n-buthyl chloride	Nitrobenzene Sodium-potassium alloy. (solvent drying agent).

Table 2.5 Materials used.

2.2.1 Purification of Monomers.

2.2.1 (a) Purification of styrene and methyl methacrylate[6]

Styrene and methyl methacrylate were each purified as follows :

1) Washing to remove inhibitor : the inhibitor, usually, an aromatic compound such as hydroquinone or t-butyl pyrocatechol, was removed by washing the monomer with a 10 % aqueous sodium hydroxide solution. Roughly equal parts of the basic solution and the monomer were placed in a separatory funnel and thoroughly mixed by tumbling. The heavier aqueous phase was then drained off. The procedure was repeated once or twice until the liquids remained clear. The monomer was then washed with distilled water until limus paper show that all of the base had been removed.

2) Drying the monomer : for this purpose, $CaCl_2$ (dehydrated-granular pure) was added to the monomer (100 g/l) with subsequent occational tumbling ; drying was complete in about 1½ hours.

3) Distillation : about 1 g/l. Cucl stabitizer was added to the monomer and the monomer vacuum distilled (60 torr) under nitrogen at 37-39°C. The apparatus was as shown in Fig. 2.1.

4) Store the monomer : using parafilm seal stop-cock and stores at 0-10°C until required.

5) Check before use : test for the presence of polymer in redistilled monomer just before use by adding to excess methanol. Turbidity indicates the presence of polymer. In our experiment, there was no polymer.

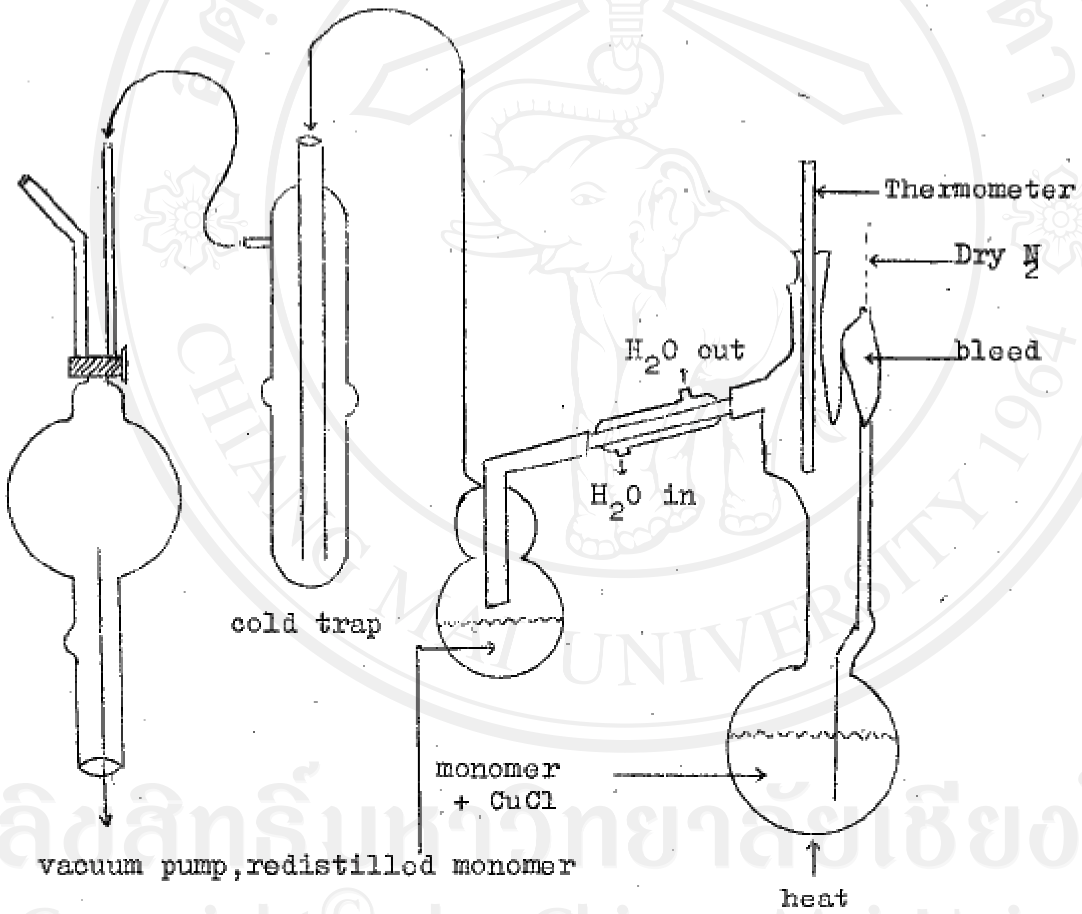


Fig. 2.1 Vacuum distillation of monomer.

2.2.1 (b) purification of Acrylonitrile.

Acrylonitrile was purified by a simple distillation technique. The boiling point fraction distilling over at 78°C was collected and stored, using a parafilm seal stopcock closure, in a cool dark place until required for use.

2.2.2 Purification of diluents and solvents.

The criteria for the purity of monomers also apply to any diluents and solvents used in a polymerization. The materials also need to be purified by distillation, cyrstallization, or the other methods previously described for monomers. Diluents for anionic polymerization are usually distilled from an excess of the initiator ; for example, tetrahydrofuran from sodium/naphthalene or benzene from butyl Lithium. Peroxides are removed from these solvents by treatment with sodium sterate.

2.2.2 (a) Purification of benzene

250 ml benzene were shaken with NaOH, filtered into a flask and a sodium-potassium alloy added for drying (preparation of the sodium-potassium alloy is described later in Section 2.2.2 (d)). The flask and its contents were then left overnight as shown in Fig. 2.2.

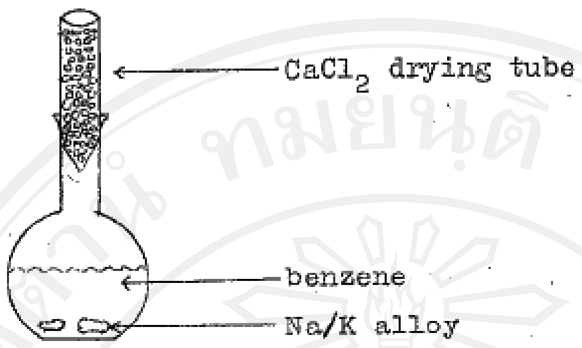


Fig. 2.2 Drying of benzene using Na/K alloy.

After overnight drying, the benzene was then distilled into a flamedried flask after the addition of more of the sodium-potassium alloy (See Fig. 2.3 below).

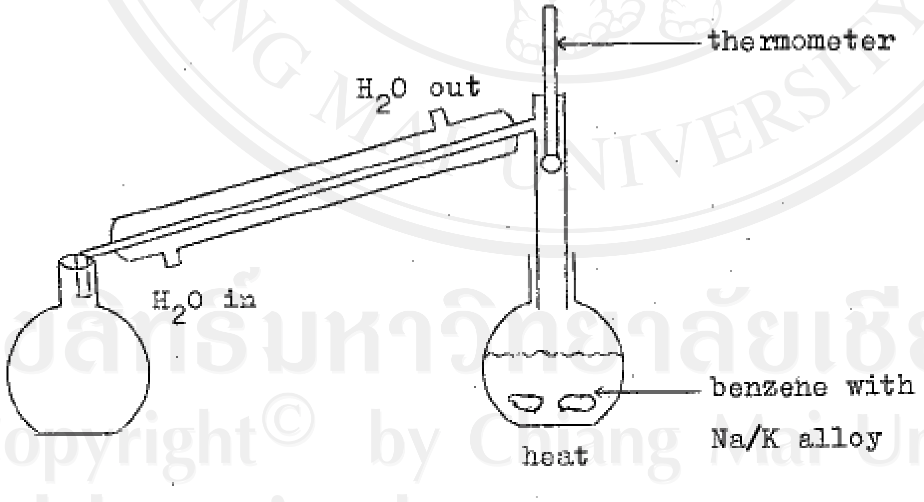


Fig. 2.3 Diagram of simple distillation.

2.2.2 (b) Purification of n-heptane

N-heptane was dried using the sodium-potassium alloy and left overnight as in Fig. 2.2 previously. Then after adding more of the sodium-potassium alloy, it was distilled into a flame-dried flask as shown in Fig. 2.3.

2.2.2 (c) Purification of nitrobenzene.

Nitrobenzene was purified by a simple distillation procedure.

2.2.2 (d) Preparation of sodium-potassium alloy.

The sodium-potassium alloy was prepared by taking sodium metal (1 part) and potassium metal (5 parts), heating under xylene until molten and using a stirring rod to mix carefully. After allowing to cool, the alloy, still in liquid form, was transferred by means of a pipette. Finally, after use, the alloy was destroyed by pouring into butanol, in a well-ventilated open area, followed by treatment with water.

2.2.3 Purification of Initiators/Catalyst Reagents.

2.2.3 (a) Purification of benzoyl peroxide.

Benzoyl peroxide was purified by dissolving in cold chloroform followed by re-precipitation from excess methanol.

2.2.3 (b) Purification of n-butyl chloride.

N-butyl chloride, for later use in preparing the n-butyl Lithium anionic initiator, was purified according to the procedure outlined for benzene and n-heptane previously.

2.3 Copolymerization techniques.

2.3.1 Free radical copolymerization.

2.3.1 (a) Calculation of the monomer mixture composition for free radical copolymerization.

From the copolymer composition equation:

$$\frac{d[M_1]}{d[M_2]} = \frac{m_1}{m_2} = \frac{[M_1]}{[M_2]}\left(\frac{r_1 \quad [M_1] \qquad [M_2]}{r_2 \quad [M_2] + [M_1]}\right)$$

where m_1 = concentration of methyl methacrylate in copolymer

m_2 = concentration of styrene in copolymer

$[M_1]$ = concentration of methyl methacrylate in monomer mixture

$[M_2]$ = concentration of styrene in monomer mixture.

Hence, for, for example, a copolymer of composition:

Hence for :-

Methyl methacrylate : 0.00938 moles are contained in 1 ml.

Methyl methacrylate : 1.00 mole is contained in $\frac{1.00 \times 1}{0.00938}$

$= 106.61$ ml.

Similarly, for :-

Styrene : 0.00871 moles are contained in 1 ml.

Styrene : 6.32 moles are contained in $\frac{6.32 \times 1}{0.00871} = 725.60$ ml.

Totle volume of the monomer mixture is 832.21 ml.

if monomer mixture = 832.21 ml. and methyl methacrylate used

$= 106.61$ ml.

then, for a monomer mixture = 50 ml., methyl methacrylate used

$= \frac{106.61 \times 50}{832.21}$

$= 6.41$ ml.

Similarly, for styrene :-

if monomer mixture = 832.21 ml. and styrene used $= 725.60$ ml.

then, for a monomer mixture = 50 ml., styrene used $= \frac{725.60 \times 50}{832.21}$

$= 43.59$ ml.

Thus, in this way, the relative volumes of methyl methacrylate and styrene required in the initial monomer feed in order to produce a range of copolymer compositions can be easily calculated (See Table 2.7).

Copolymer composition MMA : ST.	Volume of MMA used, ml.	Volume of ST used, ml.	Copolymerization time, hr.
0 : 100	-	50	4
20 : 80	6.41	43.59	4
40 : 60	17.53	32.59	4
50 : 50	24.85	25.15	4
60 : 40	32.27	17.73	4
75 : 25	41.14	8.86	4
80 : 20	43.45	6.55	4
100 : 0	50	-	4

Table 2.7 The calculated monomer volumes required for a range of MMA : ST free radical copolymer composition.

2.3.1 (b) Free radical copolymerization procedure[7]

In a 50 ml. tube was placed 50 mg. of benzoyl peroxide. After deaeration the tube using a suitable adaptor

(See Fig. 2.4) for evacuation and subsequent charging with nitrogen, 50 ml. of the appropriate monomer mixture (according to Table 2.7) was added with a pipette. Under a slight excess pressure of nitrogen the adaptor was then replaced with a ground-glass stopper and the tube placed in a thermostat at 60°C. After 4 hours, the contents of the tube were added dropwise to 500 ml. of methanol with constant magnetic stirring. After filtration using a sintered glass filter, the resultant copolymer was washed with methanol, reprecipitated twice from benzene and finally dried in vacuo at 60°C.

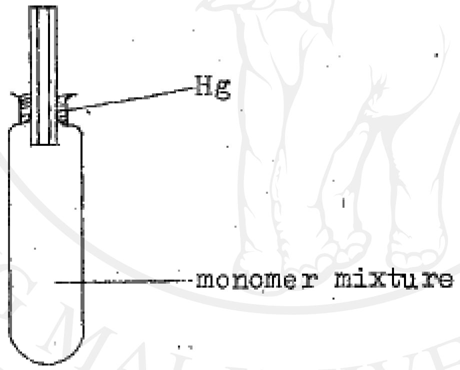


Fig. 2.4 Dilatometer used for copolymerization.

2.3.2 Anionic Copolymerization[8]

2.3.2 (a) Preparation of initiator (n-butyl Lithium).

Into a 250 ml. conical flask, equipped with seal and magnetic stirrer bar and initially charged with nitrogen, was added 220 ml. n-heptane and 20 ml. n-butyl chloride until the flask was full (See Fig. 2.5). Small pieces of freshly cut lithium metal (3.5 g.) were then added to the solution mixture and the flask sealed and left stirring overnight. On allowing to settle, the solution mixture was black and cloudy in appearance, indicating formation of the n-butyl lithium.

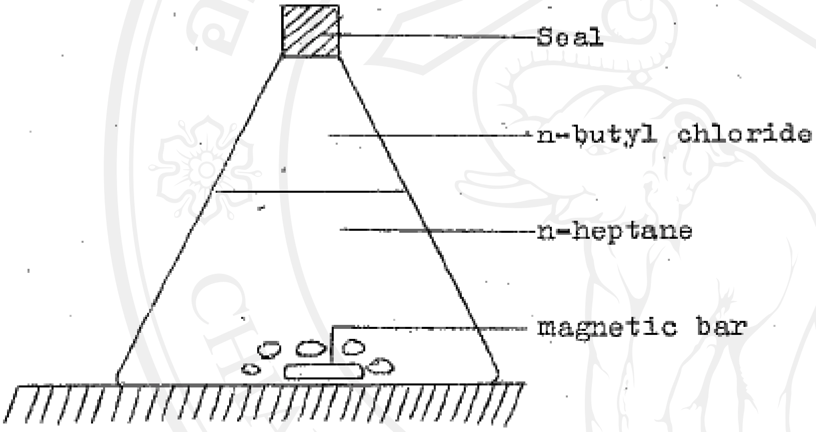


Fig. 2.5 Preparation of n-butyl lithium.

MMA used, ml.	ST used, ml.
1.0	9.0
3.0	7.0
5.0	5.0
7.0	3.0

Table 2.8 Monomer volumes of MMA and ST used for anionic copolymerization.

2.3.2 (b) Anionic copolymerization procedure.

In a 50 ml. flask, flamed dry and charged with nitrogen, was placed 10 ml. of the monomer mixture prepared according to Table 2.8 above. The flask was stopped with a self-sealing cap (See Fig. 2.6) and, after cooling to -50°C, 2 ml. of the freshly prepared n-butyl lithium solution were injected with a hypodermic syringe. The reaction mixture was maintained at -50°C with stirring for 90 minutes before being diluted with 25 ml. of benzene. The copolymer was then precipitated by adding the solution dropwise to 300 ml. of methanol. The copolymer obtained was finally treated as described previously under free radical copolymerization.

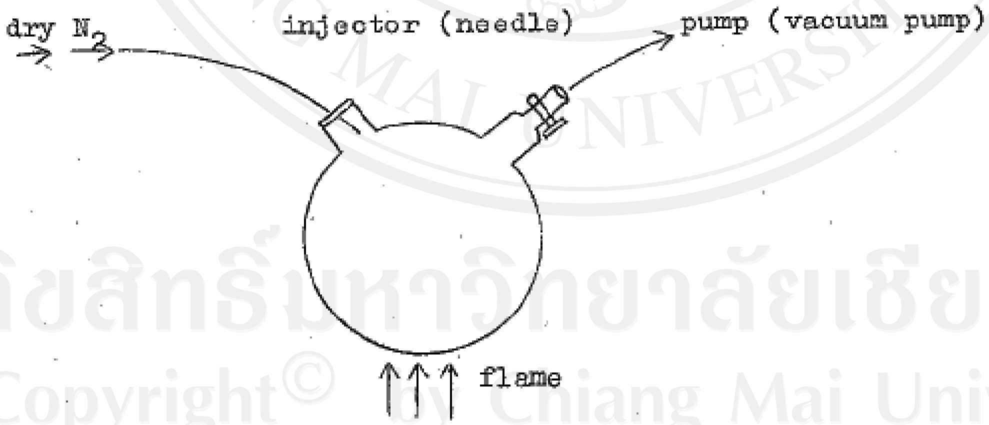


Fig. 2.6 Ground-neck flask equipped with self-sealing stopper.

2.3.3 Cationic Copolymerization[9]

A 100 ml. flask equipped with a septum adaptor (See Fig. 2.6) was flame-dried under vacuum and subsequently charged with nitrogen. Then, 5 ml. of a previously prepared monomer mixture (See Table 2.9) together with 40 ml. of initiator solution were added, the latter having been prepared from 50 ml. of pure, dry nitrobenzene and 300 mg. (2.25 millimoles) of anhydrous aluminium trichloride. The adapter was removed from the flask while applying a slight excess pressure of nitrogen and the flask immediately stopped and left to stand at 25°C for 1 hour. The reaction mixture was then added dropwise to 200 ml. of methanol and the copolymer precipitate treated as describe previously.

Under the above conditions, the cationic copolymerization is so rapid that even with much lower initiator concentrations nearly haff of the monomer mixture is consumed within one hour. At 50 % conversion, however, the reaction effectively stops since, with cationic initiators, practically only styrene is incorporated into the polymer chains.

MMA used, ml.	ST used, ml.
1.5	3.5
2.5	2.5
3.5	1.5
4.0	1.0

Table 2.9 Monomer volumes of MMA and ST used for cationic copolymerization.

2.4 Instrumental techniques.

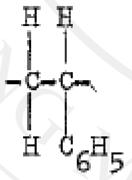
Amongst the techniques which are commonly used to analyse polymers are infrared spectroscopy (IR), nuclear magnetic resonance spectroscopy (NMR) and differential scanning calorimetry (DSC). Two of these techniques which have been utilized in this study-namely, infrared spectroscopy and nuclear magnetic resonance spectroscopy are now described.

2.4.1 Infrared analysis of polymers.

2.4.1 (a) Introduction[10]

The absorption of radiation between wave numbers 4000 to 660 cm^{-1} cause stretching and vibrations of bonds in polymer molecules. The motions for any specific functional group are essentially independent of the rest of the molecule and comparable to these observed for low molecular weight compounds with similar structures (model compounds). The characteristic band frequencies are related to degrees of freedom which are distributed as rotational, translational, and vibrational motions. These motions are in related to the number of atoms in simple molecules or to the number of atoms in the mer or repeat unit in a polymer molecule.

Thus, a polymer such as polystyrene may be considered to be similar to a molecule with 16 atoms



$$-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{C_6H_5}{C}}-$$

Since it has no symmetry, all vibrations are active, i.e., 3 degrees of rotational freedom, 3 degrees of translational freedom, and 42 degrees of vibrational feedom (3n-6). As in the case of simple molecules, these motions are characteristic of the groups present, and a sufficient number of band frequencies may be readily observed to assure proper identification of this polymer.

The infrared spectrum of polystyrene shown in Fig. 2.7 is used as a standard for the calibration of infrared spectrophotometers. This spectrum shows typical C-H stretching vibrations at 3.3, 3.4, and 3.5 μ ; C-C stretching vibrations are shown at 6.2 and 6.7 μ ; and out-of-plane bending of the C-H bonds in the benzene rings may be observed at 11.0 and 14.3 μ. The bands at 8.7 and 9.7 μ are said to be in the "finger print" region. These are characteristic of polystyrene but their origin is not readily determined.

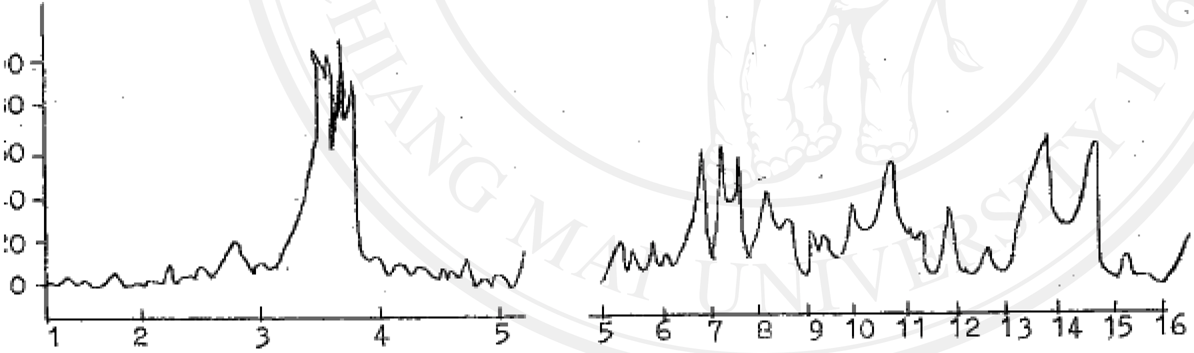


Fig. 2.7 Infrared spectrum of polystyrene film.

Absorption bands for typical functional groups are shown in Table 2.10 The absorption bands for carbon-chlorine, nitrile, hydroxyl, and carbonyl may be used to identify polymers containing these functional groups. The intensity of the carbonyl absorption band at about 5.9 μ may be used to ascertain the extent of deterioration of polymers by oxidative degradation.

The extent of branching in polyethylene may be ascertained by measuring the relative absorbance of the methylene and methyl groups. The relative intensity of absorption for characteristic bands for cis-1, 4-dienes, trans-1, 4-dienes, and 1, 2-dienes has been used to determine the relative amounts of these structures in synthetic polydienes.

The degree of isotacticity of samples of poly (methyl methacrylate), polypropylene, polystyrene, and poly(vinyl methyl ether) has been estimated from the ratios of characteristic absorbance bands related to tacticity. Anton

Group	Type of vibration	Wavelength	Wave number, , cm^{-1}
CH_2	Stretch	3.38-3.51	2850-2960
	Bend	6.82	1465
	Rock	13.00-13.80	725-890
CH_3	Stretch	3.38-3.48	2860-2870
	Bend	6.9	1450

Table 2.10 (Continued)

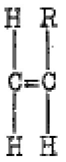
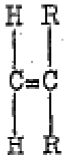
Group	Type of Vibration	Wavelength	Wave number, , cm^{-1}
 $\overset{H\ \ R}{\underset{H\ \ H}{C{=}C}}$	C-H stretch	3.25-3.30	3030-3085
	C-H bend in plane	7.10-7.68	1300-1410
	C-H bend out of plane	10.10-11.00	910-990
	C-C stretch	6.08	1643
 $\overset{H\ \ R}{\underset{H\ \ R}{C{=}C}}$	C-H stretch	3.24	3080
	C-H bend in plane	7.10	1410
	C-H bend out of plane	11.27	888
	C-C stretch	6.06	1650
Benzene	C-H bend out of plane	14.50	690
OH	stretch	2.7-3.2	3150-3700
SH	stretch	3.9	2550
Aliphatic acid	C=O stretch	5.85	1710
Aromatic acid	C=O stretch	5.92	1690
CCl	stretch	12-16	620-830
CN	stretch	4.8	2200

Table 2.10 Absorption bands for typical groups in polymers.

determined thermal transition temperatures of polyamides, polyesters, polystyrene and poly (vinyl acetate) by monitoring thermal-sensitive absorption bands in the 900 to 1100 cm^{-1} region.

The random copolymers of methyl methacrylate and styrene[11] tend to have rather similar spectra to that of polystyrene alone and are themselves rather similar to each other. In this case, the presence of the mono-substituted benzene ring is evident from the bands at 13.3 μm and a further weak but sharp aromatic band appears at 6.25 μm. The presence of ester is evident from the 5.8 μm carbonyl band whilst the C-O structure has the characteristic methacrylate pattern (7.9 μm, 8.1 μm, 8.4 μm and 8.7 μm). However, in copolymers, these C-O bands are broader and less well defined than in polymethyl methacrylate. The major differences in the spectra of these copolymers lie between 9 μm and 10 μm and beyond 12 μm.

Block copolymers of methyl methacrylate and styrene and mixtures of these two resins may also be distinquished from the equivalent random copolymers. When the amount of polystyrene is in the range 0 to 20 %, there is a significant difference in the position of the styrene absorption band near 14.3 μm. In black copolymers and blends, this occurs at 14.33 μm, while in random copolymers it moves to 14.25 μm. However, this difference is not apparent at high styrene contents, but here the broadening of the C-O structure of the methyl methacrylate, which is evident in random copolymers, does not occur in blends or block copolymers.

In the spectrum of styrene/acrylonitrile copolymer, the major features arise from styrene, but acrylonitrile is evident at 4.4 μ m. Measurement of the absorbance ratio of the bands at 4.4 μ m. and 6.25 μ m, due to acrylonitrile and styrene respectively, appears to be a satisfactory method of estimating the composition of this copolymer, using reference samples of known composition for calibration.

2.4.2 (b) Quantitative determination of the methyl acrylate content of methyl acrylate/methyl methacrylate copolymers by infrared spectroscopy[12]

This method is suitable for copolymers containing 2 % to 20 % methyl acrylate ; standard samples of known composition being required for calibration purposes.

All standards and test samples are prepared as films of 0.002 in (0.05 mm.) thickness by pressing between polytetrafluoroethylene coated plates. The spectra of all samples are then recorded over the range 11 μ m to 13 μ m along with that of a sample of methyl methacrylate homopolymer. The spectrum of a given copolymer will be similar to that shown in Fig. 2.8 below:

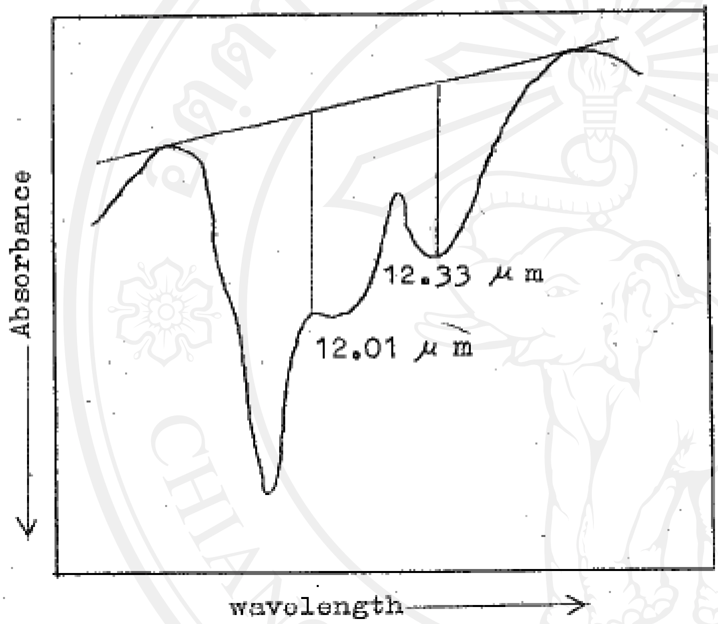


Fig. 2.8 Infrared spectrum of methyl methacrylate/methyl acrylate (90:10) copolymer

The background absorbance is drawn tangentially as shown in the figure and the absorbance at the methyl acrylate wavelenght (12.01 μ m) and at the methyl methacrylate wavelength (12.33 μ m) measured.

The absorbance ratio

$$\frac{\text{Absorbance at } 12.01\,\mu\text{m}}{\text{Absorbance at } 12.33\,\mu\text{m}}$$

is then plotted against the corresponding concentration ratio

$$\frac{\text{Methyl acrylate}}{\text{Methyl methacrylate}}$$

for all standards, including the methyl methacrylate homopolymer. The plot should be linear with an intercept on the absorbance axis at the value for the methyl methacrylate homopolymer. This graph is then used to determine the composition of unknown samples from their appropriate absorbance ratios.

For semi-quantitative work, absorbances measured from Figure 2.8 may be used, together with the corresponding data on methyl methacrylate homopolymer to construct a calibration graph.

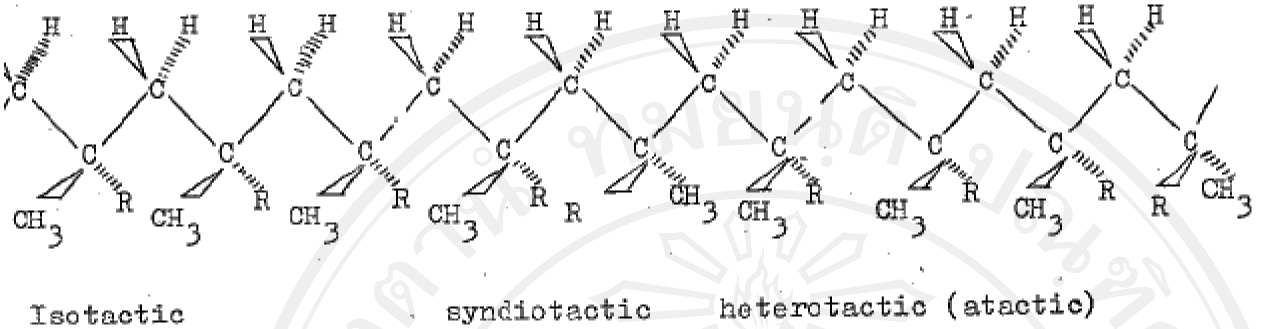
2.4.2 Nuclear magnetic resonance analysis of polymers[13]

2.4.2 (a) Introduction.

The major application of NMR spectroscopy in polymers is in the study of chain configurations and microstructure. Here NMR is probably the most powerful tool available, with the possible exception of X-ray diffraction in the case of polymer in which crystallinity is highly developed. This recent expansion of the utility of NMR has resulted from the development of techniques for observing so-called narrow-line spectra observed a few years ago. In broad-line work, NMR provides a useful method for studying molecular motion in solid polymers, equalling the utility of the older methods of dynamic mechanical testing and dielectric studies. NMR, however, has the added advantage in that it allows study of the motion and positions which are not readily detected by most other means.

2.4.2 (b) Nuclear magnetic resonance analysis of polymers.

High resolution NMR has proved to be a particularly useful tool in the study of the microstructure of polymers in solution where the extensive molecular motion reduced the effect of long range interactions and allows the short range effects to dominate. Interpretation of chain tacticity, based on the work of Bovey and Tiers, can be illustrated using poly (methyl methacrylate) as an example. The three possible steric configurations are shown in Figure 2.9where R is the acetate group-$COOCH_3$.


Isotactic syndiotactic heterotactic (atactic)

ig. 2.9 Stereoregular triads for poly (methyl methacrylate), where $R = -COOCH_3$.

For the purposes of NMR measurements, three consecuive monomer units in a chain are considered to define a configuraion and are called a "triad". The term "heterotactic" is used now o define a triad which is neither isotactic nor syndiotactic. In he structures shown, whilst the three equivalent protons of the c-methyl group absorb radiation at a single frequency, this freuency, this frequency is different for each of the three kinds of riad, due to the environment of the α -methyl groups in each being ifferent. For poly (methyl methacrylate) samples which were repared under different conditions to give the three forms, resoance at τ = 8.78, 8.95 and 9.09 were observed, which were assiged to the isotactic, heterotactic, and syndiotactic triads respecively. Thus, in a sample with a mixture of configurations a triple peak will be observed and the area under each of these peaks will correspond to the amount of each triad present in the polymer chain. This is illustrated in Figure 2.10 where one sample is predominantly isotactic but also contains smaller percentages of the heterotactic and syndiotactic configurations.

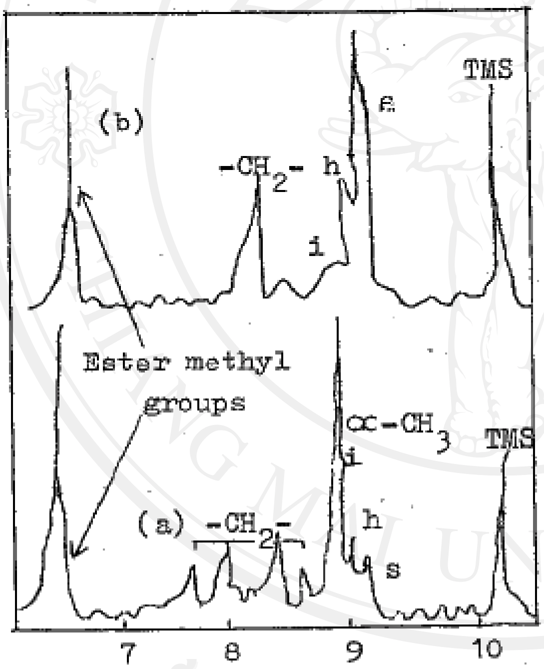


Fig. 2.10 NMR spectra for (a) an isotactic sample and (b) a predominantly syndiotactic sample of poly (methyl methacrylate).

The analysis can be carried further. The fraction of each configuration, P_i, P_h and P_s, measured from the respective peak areas, can be related to p_m, the probability that a monomer adding on to the end of a growing chain will have the same configuration as the unit it is joining. This leads to the relations.

$$P_i = p_m^2, \; P_s = (1-p_m)^2, \text{ and } P_h = 2p_m(1-p_m).$$

Curves plotted according to this simple analysis are shown in Fig. 2.11 where they are compared with experimental data obtained for various tactic forms of poly (α -methyl styrene).

Differences in the microstructure of polydienes and copolymers can also be made using NMR. In the polydienes, the difference between 1, 2-and 1, 4-addition can be distinguished on examination of the resonance peaks corresponding to terminal olefinic protons, found at $\tau = 4.9$ to 5.0, and non-terminal olefinic protons, observed at $\tau = 4.6$ to 4.7.

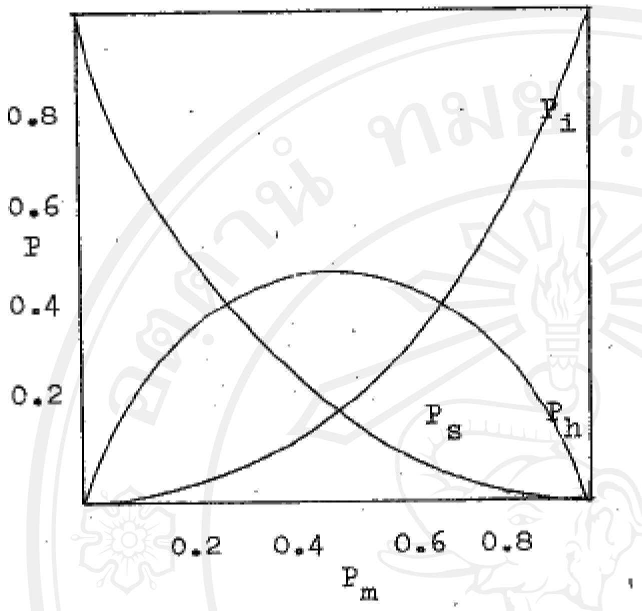


Fig. 2.11 Theoritical curves for P as a function of p_m for each of the three configurations. Points represent experimental data for poly (2-methyl styrene) and illustrate the validity of the analysis.[14]

2.4.2 (c) Quantitative analysis of acrylic copolymers from the NMR spectrum.[15]

The NMR spectrum of a methyl methacrylate/styrene copolymer is as shown in Figure 2.12. The resonances of the aryl protons are seen near 3 τ. The methoxy resonance is of particular interest as it appears within the rather wide range of 6.5 τ to 7.6 τ depending upon the environment of the group. It is possible to calculate from the reactivity ratio of the two monomers the relative proportions of the triad sequences MMM, MMS, and SMS in a copolymer and to relate these to the relative areas of resonances in this region of the spectrum. From this it may be deduced that the resonance near 6.5 τ arises from the methoxyl protons of the central M unit in the sequence MMM, that near 7.2 τ from MMS and finally that a resonance near 7.6 τ (which is very weak in Figure 2.12) arises from the M unit in the triad SMS. This assignment appears resonable, as one would expect the resonance to move to higher field with decreasing polarity of the environment. Additional structure appears on each of these resonances because isotactic syndiotactic and heterotactic arrangements are possible in each case and these have a small but observable effect on the positions of the resonances.

The quantitative analysis of such a copolymer is relatively straightforward. The low field resonance near 3 τ is due to the 5 protons of the benzene ring of styrene. For each 5 aromatic protons there are 3 protons in the aliphatic proton of the styrene molecule.

Hence, if the area of the aromatic resonance at about 3 τ is A, and the area of the remaining resonances due to the copolymer as a whole be B, Then, of the latter area 3A/5 is due to styrene.

Hence, (5B-3A)/5 is due to the resonance of the protons of methyl methacrylate. For each A/5 molecules of styrene combined in the copolymer there are (5B-3A)/(5x8) molecules of methyl methacrylate (because there are 8 aliphatic protons in the methyl methacrylate repeat unit in the copolymer).

Hence,

$$\frac{\text{Molar concentration of styrene}}{\text{Molar concentration of methyl methacrylate}} = \frac{A}{5}\,\frac{5\text{x}8}{5B-3A}$$

$$= \frac{8A}{5B-3A}$$

from which the w/w ratio may be calculated.

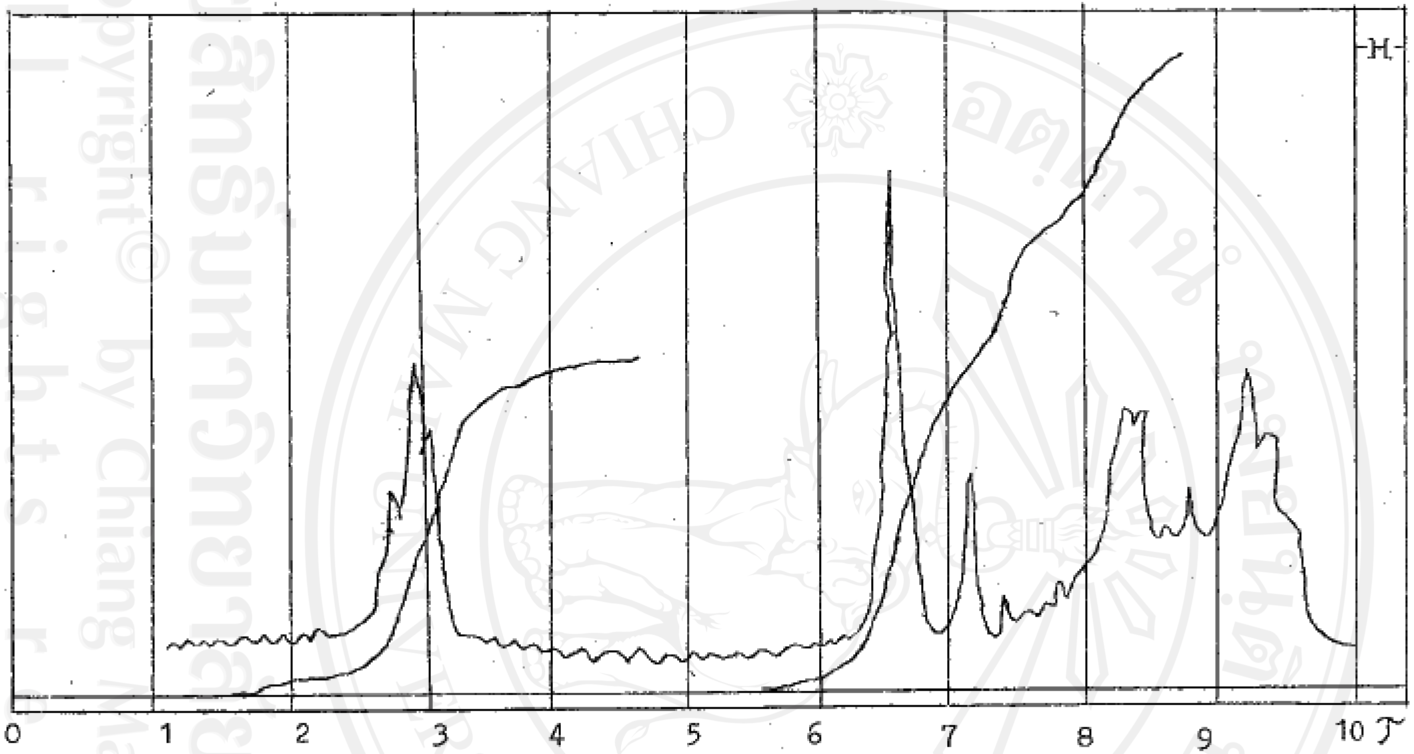


Fig. 2.12 NMR spectrum of methyl methacrylate/styrene (70:30) copolymer at 100MHz in deuterochloroform at room temperature.