763. *Liquid-phase Reactions at High Pressure. Part XII.*[1] *The Polymerisation Ceiling Temperature of α-Methylstyrene at High Pressures.*

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The ceiling temperature for polymerisation of α-methylstyrene is increased from 61° at 1 atm. to 171° at 6480 atm. The variation with pressure is linear and of the magnitude expected from the effect of pressure on the rates of propagation and depropagation. The polymerisation rate depends on catalyst concentration in the same way as that of styrene, but it reaches a maximum with increasing pressure and decreases at the highest pressures. This is attributed either to a phase separation or to a decrease in the rate of propagation at high viscosities.

AT low temperatures α-methylstyrene is readily converted by ionic catalysts into polymers of high molecular weight. Hersberger, Reid, and Heiligmann[2] report molecular weight of 84,000 (aluminium chloride in ethyl chloride at −130°), and Okamura and his co-workers[3] record molecular weights from 350,000 to 1,000,000 (boron trifluoride–ether complex in hexane–chloroform mixture at −78°). At room temperature polymers having a molecular weight from 300—400 up to 3000—4000 are usually produced, although a figure of 339,000 has been obtained[4] from the sodium-catalysed polymerisation at 10°.

The methyl substituent impedes radical-polymerisation, which has sometimes been stated not to occur, but Lowry[5] has recently measured the low rates of reaction in three free-radical systems at 25° and 30°.

The heat of polymerisation is only about 8 kcal./mole, in agreement with the theory that α-methylstyrene displays a ceiling-temperature phenomenon of the type recently reviewed by Dainton and Ivin.[6] At this temperature depropagation is faster than chain

[1] Part X, *J.*, 1956, 953; Part XI, *Discuss. Faraday Soc.*, 1956, **22**, 122.
[2] Hersberger, Reid, and Heiligmann, *Ind. Eng. Chem.*, 1945, **37**, 1073.
[3] Okamura, Higashimura, and Imanishi, *J. Polymer Sci.*, 1958, **33**, 491.
[4] Jones, Friedrich, Werkema, and Zimmerman, *Ind. Eng. Chem.*, 1956, **48**, 2123.
[5] Lowry, *J. Polymer Sci.*, 1958, **31**, 187.
[6] Dainton and Ivin, *Trans. Faraday Soc.*, 1950, **46**, 331; *Quart. Rev.*, 1958, **12**, 61.

growth, and polymer formation is impossible. The existence of a propagation–depropagation equilibrium has been demonstrated for α-methylstyrene in the range —40° to 0° by Worsfold and Bywater [7] who used the sodium-naphthalene catalyst in tetrahydrofuran, so that termination was negligible. McCormick,[8] for the same system, determined the ceiling temperature to be 61°, and Brown and Mathieson [9] estimate 60° from their experiments with trichloroacetic acid as catalyst in ethylene dichloride. The results of various kinetic studies [9,10] indicate that, while the depropagation fixes the upper temperature limit, in most instances other processes of termination and transfer determine the molecular weight and the production of very low polymer.

The demonstration of a ceiling temperature at 61° and ordinary pressure is particularly interesting in connection with the results of Sapiro, Linstead, and Newitt.[11] These authors, using pressures of from 2000 to 10,000 atmospheres, obtained polymers of α-methylstyrene (M, 1170—5800) at 100—125°, although not at 150°. This indicates that high pressures raise the ceiling temperature for polymerisation, an effect which is to be expected on theoretical grounds. A more detailed study of the polymerisation at pressures up to 11,800 atm. and temperatures up to 170° has therefore been made.

EXPERIMENTAL

Apparatus.—The vessel was a vertically mounted steel cylinder (diameter 6″ outside, 0·6″ inside), of auto-frettaged monobloc construction. It was filled with liquid paraffin in which pressure was developed by a hand-pump acting through a differential piston intensifier. It was heated electrically and the temperature controlled by a mercury contact thermometer between the heating-jacket and the cylinder. There was a small temperature gradient along the axis of the cylinder but the temperatures at the ends of the reaction tube (immersed in the paraffin) were within ±1° of the recorded mid-point values. In preliminary experiments with benzoyl peroxide as initiator a glass reaction tube with a mercury seal was employed, but a white precipitate appeared at the mercury surface (also reported by Walling and Pellon [12]). For subsequent work we used Fluon tubes (0·25″ outside diameter, 0·03″ wall thickness) sealed with tapered plugs of the same material at each end. Pressure was transmitted through the flexible tube wall.

Materials.—α-*Methylstyrene.* 95—99% pure material (200 ml.) was washed with 10% sodium hydroxide solution (3 × 100 ml.) to remove quinol inhibitor, then six times with distilled water, dried ($CaCl_2$), and distilled under a vacuum. The middle 60% was retained (b. p 54·5—55·0°/14 mm.; $n_D^{17·4}$ 1·5384) and was kept under nitrogen. The monomer did not give a precipitate in methanol after 7 days, but a new batch was purified every 48 hr.

Azodi-isobutyronitrile. Material recrystallised from chloroform, dried under a vacuum, and kept in the dark, had m. p. 106°.

Benzoyl peroxide. The peroxide, precipitated from chloroform, dried under a vacuum, and kept in the dark, melted at 105°.

Di-t-butyl peroxide. This peroxide, supplied 98% pure, was distilled under a vacuum (nitrogen) and kept in the dark under a vacuum at 0°. It had n_D^{20} 1·3890.

Trichloroacetic acid. The " AnalaR " product was twice recrystallised from benzene, dried, and kept under a vacuum. It had m. p. 58°.

Toluene. " Sulphur-free " toluene was distilled and the middle 60% (b. p. 110·6°) retained.

Methanol and 1,2-epoxypropane. These were " AnalaR " materials.

Separation of Solid Polymer.—The reaction product was dissolved in 1,2-epoxypropane (25 ml.), and the solution added dropwise, with constant stirring, to cold methanol. The precipitated polymer was coagulated by gentle heat, filtered on sintered glass, washed with solvent mixture and dried at 60° for 24 hr.

Separation of Liquid Polymer.—The precipitation method separates pentamer and higher

[7] Worsfold and Bywater, *J. Polymer Sci.*, 1957, **26**, 299; *Canad. J. Chem.*, 1958, **36**, 1141.
[8] McCormick, *J. Polymer Sci.*, 1957, **25**, 488.
[9] Brown and Mathieson, *J.*, 1958, 3445, 3507.
[10] Worsfold and Bywater, *J. Amer. Chem. Soc.*, 1957, **79**, 4917.
[11] Sapiro, Linstead, and Newitt, *J.*, 1937, 1784.
[12] Walling and Pellon, *J. Amer. Chem. Soc.*, 1957, **79**, 4776, 4782, 4786.

polymers. The amount of lower polymer in a few samples was determined by the frozen-solvent method,[13] dioxan being used. The solid dioxan was sublimed at 4 mm. and the samples attained constant weight in 12 hr.

RESULTS AND DISCUSSION

A. Dependence of Polymerisation Rate on Initiator Concentration.—Sapiro *et al.*[11] did not observe any dependence of rate on initiator concentration, so measurements with benzoyl peroxide initiator were carried out to establish the relationship. The results are shown in Table 1. Logarithmic plots of initiator concentration against mean rate were found to be good straight lines at each of the two pressures used so that the rate is proportional to [Initiator]^x, where x is 0·44 and 0·45 at 8100 and 9000 atm. respectively.

TABLE 1. *Dependence of rate on initiator concentrations.*

(Each run of 4 hr. duration at 94·5°.)

8100 atm.			9000 atm.		
Wt. % of benzoyl peroxide	Wt. % of solid polymer	Mean rate (%/min. × 10³)	Wt. % of benzoyl peroxide	Wt. % of solid polymer	Mean rate (%/min. × 10³)
Nil	1·06	4·4			
0·385	3·24	13·5	0·132	1·44	6·0
1·091	4·87	20·3	0·243	3·33	8·0
1·396	5·55	23·2	1·110	3·74	15·6
2·181	7·14	28·9	1·641	3·82	15·9
2·180	6·90	28·8	2·190	4·80	20·0

A small error is involved in the use of mean rates, and it should be noted that the measurements were made in the region in which the rate decreases with increasing pressure (discussed in section C, below). The value of x, when termination results from encounters between two radicals should be 0·5, but Merrett and Norrish[14] found that it decreased from 0·50 at 1 atm. to 0·40 at 3000 atm. in the benzoyl peroxide–styrene system at 60°, and Nicholson and Norrish[15] record a decrease from 0·50 to 0·45 for the same system and pressure range at 30°. The relation between rate and [Initiator] is thus similar for α-methylstyrene and styrene.

B. The Ceiling Temperature at High Pressures.—A few experiments at 4550 atm. without initiator gave results in accordance with those of Sapiro *et al.* The yield of solid polymer increased from 20·8% at 95° to 61·7% at 112° (22 hr.), but only 2·1% was formed in 96 hr. at 141°.

For the systematic measurement of ceiling temperatures an initiator was used, and di-t-butyl peroxide was selected because it does not decompose too rapidly at the experimental temperatures. The half-life of the initiator[16] at 1 atm. is about 220 hr. at 100°, 2·25 hr. at 140°, and 0·125 hr. at 170°. The values are probably at least twice as great at high pressure. The yield of solid polymer in runs of 4 hr. duration (occasionally longer or shorter) was determined over a range of temperatures at four pressures, and the results are

TABLE 2. *Polymerisation ceiling temperatures at high pressures.*

Pressure (atm.)	2200	4210	4860	6480
Ceiling temp. (c)	97°	131°	143°	171°

shown in Fig. 1. From the curves it will be seen that at each pressure the yield of solid polymer first increases with temperature then passes through a maximum and falls rapidly to zero. The ceiling temperatures (the points at which the curves cut the temperature axis), are given in Table 2.

[13] Lewis and Mayo, *Ind. Eng. Chem. Analyt.*, 1945, **17**, 134.
[14] Merrett and Norrish, *Proc. Roy. Soc.*, 1951, *A*, **206**, 309.
[13] Nicholson and Norrish, *Discuss. Faraday Soc.*, 1956, **22**, 97, 104.
[16] Offenbach and Tobolsky, *J. Amer. Chem. Soc.*, 1957, **79**, 278.

The relation between ceiling temperature and pressure is linear, and extrapolation to 1 atm. gives a ceiling temperature of 60°, in good agreement with McCormick's and Brown and Mathieson's values.

The analogy between polymerisation ceiling temperatures and physical aggregation processes has been pointed out.[6] If an equation of the same form as the Clausius–Clapeyron relation, $dT/dP = T\Delta V/\Delta H$, is assumed, and a value of $-8\cdot4$ kcal./mole is taken [17] for ΔH, then ΔV, the volume change for the polymer–monomer equilibrium is $-14\cdot7$ c.c./mole. This figure agrees with the value $-14\cdot1$ c.c./mole for the overall volume change at 20°, which was found by comparison of the densities of pure monomer and of a 6% solution of polymer in monomer. It is also of the order of magnitude expected from the estimated volumes of activation, ΔV^*, for propagation and depropagation. ΔV^* for
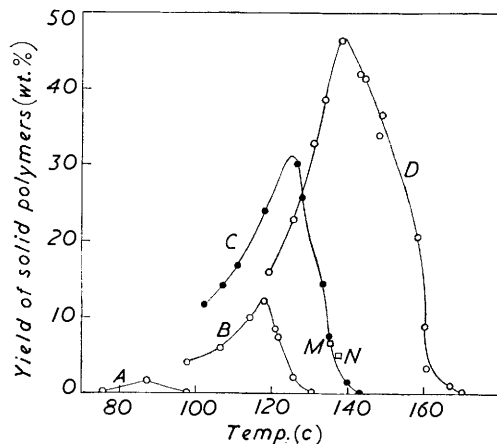

FIG. 1. *The dependence of yield of polymer on temperature at various pressures.*

A, 2200 atm.
B, 4210 atm.
C, 4860 atm.
D, 6480 atm.
M, 42 hr.
N, 44 hr.

propagation will probably be similar to the value for styrene,[18] which is $-13\cdot4$ c.c./mole. ΔV^* for depropagation is more difficult to estimate, but if, as a first approximation, a 10% stretching of the C–C bond is assumed in the activated state, and the molecular cross-section is supposed constant, a value of about $+4$ c.c./mole is obtained. The estimated equilibrium ΔV is then about -17 c.c./mole, which is sufficiently close to the experimental values for the change of ceiling temperature with pressure to be ascribed to the differential effect on the velocity of propagation and depropagation. Propagation which involves bond-formation and has a negative volume of activation is accelerated, but depropagation, which is a process of bond-breaking and has a positive volume of activation, is retarded.

The approximate molecular weights (found cryoscopically in benzene) of the solid polymers formed at 4860 atm. and at various temperatures are given in Table 3. The

TABLE 3.

Temp. (c)	107·0°	118·2°	126·8°	128·0°	133·4°	135·1°	135·3°
Mol. wt.	1120	1940	1470	1140	1110	670	580

decrease as the ceiling temperature is approached agrees with theoretical prediction [6] but is probably determined by the speed of transfer and termination, as well as by depropagation.

The liquid polymer also produced rapidly decolorised bromine in carbon tetrachloride and is identified as unsaturated dimer (cryoscopic M, 240; unsaturated dimer requires M, 236). The amount of dimer increases with reaction temperature, as shown in Table 4.

[17] Jessup, *J. Chem. Phys.*, 1948, **16**, 661.
[18] Whalley, *Discuss. Faraday Soc.*, 1956, **22**, 146.

TABLE 4. *Yield of dimer at 4860 atm. and various temperatures.*

(1·31 wt. % di-t-butyl peroxide.)

Temp. (c)	131·4°	136·0°	136·5°	150·0°	150·0°
Dimer (wt. %)	13·9	17·4	20·0	26·0	56·2
Time (hr.)	4	4	4	4	21

A large yield of dimer is obtained above the ceiling temperature for solid polymer (143° at 4860 atm.). The reason may be that the dimer has a higher ceiling temperature,[6] and there is evidence that the heat of dimerisation is greater than the heat of polymerisation to longer chains.[9,17] An alternative possibility is that at the higher temperatures transfer reactions with allylic hydrogen (as in the case of allyl acetate [12]), involving the resonance-stabilised radical $CH_2=CPh\cdot CH_2\cdot$, become important.

C. The Decreased Rate of Polymerisation at the Highest Pressures.—Table 1 shows the rate of polymerisation initiated by benzoyl peroxide at 8100 atm. to be greater than that at 9000 atm. This unexpected finding was investigated over a wider pressure range and

FIG. 2. *The effect of pressure on the rate of polymerisation, with various initiators.*

A, *Azodi-isobutyronitrile* (0·1 *mole* %).
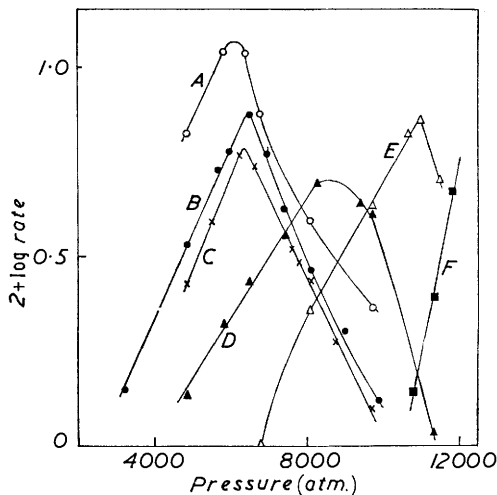B, *Benzoyl peroxide.*
C, *Di-t-butyl peroxide.*
D, *Trichloroacetic acid.*
E, *Trichloroacetic acid with 42 wt. % of benzene.*
F, *Trichloroacetic acid with 42 wt. % of toluene.*

(B—F, 1·0 *mole* %). *The rate is calculated as wt. % of solid polymer per min.*

with other initiators. The results are given in Fig. 2, in which the rates are mean rates calculated from the yields of solid polymer in 4 hr. runs at 94·5°.

At first log (rate) is proportional to pressure, as for styrene,[14] but at higher pressures it reaches a maximum and then decreases rapidly. The maximum is at a higher pressure when the monomer is diluted with 42 wt. % of benzene and does not occur in the experimental pressure range in the presence of 42 wt. % of toluene. The ceiling temperature is 94·5° at 2070 atm., so that the two effects are well removed from each other. It is known that the first-order rate constant for the decomposition of benzoyl peroxide is approximately halved at 3000 atm. and that this initiator also decomposes by a radical chain process which is accelerated by pressure and probably does not initiate polymerisation.[12,15] The decrease in polymerisation rate is not thought likely to arise from a combination of these effects as it occurs with all the initiators, including the ionic catalyst trichloroacetic acid. It is more probably the result of a large increase in viscosity or of a phase separation, both of which would be affected by dilution. The phase separation might consist of solidification of a proportion of the monomer, or of the appearance of a second, polymer-rich liquid phase containing a large fraction of the initiator, but no experimental evidence is available on this point. The effect of increased viscosity on organic bimolecular reactions has been examined by Hamann,[19] who calculated that they become diffusion-controlled and retarded if the voscosity is increased by a factor of

[19] Hamann, *Trans. Faraday Soc.*, 1958, **54**, 507.

$\sim 10^{10}$, and demonstrated this experimentally at pressures in the range 10,000—40,000 atm. The propagation reaction in vinyl polymerisation has a considerably lower activation energy than ordinary bimolecular reactions (~ 5 kcal./mole cf. ~ 20 kcal.), and the propagation rate may become diffusion-controlled if the viscosity is increased by only 10^5 or 10^6. A retardation due to increased viscosity has been observed at conversions of over 50% at ordinary pressure.[20,21]   The conversion into polymer, near the maxima of the curves in Fig. 2, ranges from 12% to 26% and probably does not increase the viscosity more than 10-fold.   The effect of pressure on the viscosity of organic liquids is very considerable, but varies markedly from one to another.   The largest increase found [22] at 6000 atm. is for eugenol, the factor being $\sim 10^4$.   It is thus possible that there is a sufficient increase in viscosity at 6000 atm. to affect the rate of polymerisation, but information about the influence of pressure on the viscosity of polymer solutions is needed to establish this.

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[20] Bengough and Melville, *Proc. Roy. Soc.,* 1955, *A,* **230**, 429.
[21] Vaughan, *Trans. Faraday Soc.,* 1952, **48**, 576; *J. Appl. Chem.,* 1952, **2**, 422.
[22] Bridgman, *Proc. Amer. Acad. Arts Sci.,* 1926, **61**, 57.