

HIGH PRESSURE POLYMERIZATION OF PERFLUOROSTYRENE

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SUMMARY

Perfluorostyrene was prepared by reaction between pentafluorophenyl-lithium and tetrafluoroethylene and its physical behavior and thermal polymerization were studied in the temperature and pressure ranges 17–155° and 6800–20 000 atm respectively. When highly superpressed the monomer becomes viscous and often glassy. The polymerization rates range from 10^{-3} to more than 10^2 per cent h^{-1} . They generally increase with temperature and pressure. Polymer intrinsic viscosities range from 0.07 to 0.41 $dl g^{-1}$. In liquid phase polymerizations they increase with pressure and decrease with temperature. In the glassy phase, polymer of lower intrinsic viscosity is formed; in the crystalline phase, higher polymer is formed.

INTRODUCTION

The synthesis of perfluorostyrene (C_8F_8) was accomplished more than a decade ago¹. Many methods now exist for its preparation. These have been recently reviewed² along with information on other related fluorostyrenes.

Perfluorostyrene, unlike styrene, is extremely difficult to polymerize. Although ring-fluorinated styrenes polymerize readily by thermal means, $\alpha\beta\beta$ -trifluorostyrene tends to form cyclic dimers and the production of high-molecular weight polymer required the development of a specific emulsion process^{3,4}. Thus, it is not surprising that with perfluorostyrene various bulk polymerization techniques failed to produce polymer. Attempted thermal polymerization in a sealed evacuated tube at 100° gave a mixture of two cyclic dimers after two years. We have found that high-pressure techniques are useful for converting many fluoromonomers into high polymers⁵. In this article the results of a study of the polymerization of perfluorostyrene in the pressure range 6800 to 20 000 atm* are reported.

* 1 atm equals 1.013×10^6 dyne cm^{-2} or 1.013×10^5 N m^{-2} .

EXPERIMENTAL

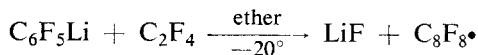
The high-pressure polymerization technique has been described previously⁶. In essence, degassed monomer was brought to the desired pressure and temperature in piston-cylinder devices. If desired, the vessel and contents were exposed to radiation of known intensity from an external cobalt-60 source. In some runs samples were encapsulated above mercury or placed in small bombs in order to conserve monomer. The monomer from the monomer-polymer mixture was removed under vacuum at 160°.

Phase behavior was studied by charging a bomb with 15 cc of monomer and measuring piston position as a function of applied force. Measurements were made on ascending and descending load at temperatures of 21, 71, 125 and 165°. Intrinsic viscosities were determined in hexafluorobenzene at 29.7°.

Monomer synthesis

Several syntheses of perfluorostyrene had been reported previous to this work but none lent itself to the preparation of large enough quantities of pure monomer^{1,7}.

About 100 g of monomer was prepared in three runs in a 30 l stainless steel tank by the reaction:



The molar ratio of pentafluorophenyl-lithium to tetrafluoroethylene to ether was 1:15:35. The pentafluorophenyl-lithium was prepared at -80° by transfer metallation of pentafluorobenzene using a 10% excess of methyl-lithium in ether. After approximately 2 h, the stoichiometric amount of methane had evolved. Tetrafluoroethylene was then added and the mixture warmed to -20°. Appearance of perfluorostyrene and disappearance of pentafluorophenyl-lithium were followed by analyzing hydrolyzed aliquots with a vapor phase chromatograph (SE-30 column at 110°). Typical data are shown in Figure 1. Pentafluorobenzene is regenerated from pentafluorophenyl-lithium on hydrolysis. The final amount of perfluorostyrene shown represents only a 10% yield despite the disappearance of 90% of the pentafluorophenyl-lithium.

After 50 h the excess tetrafluoroethylene was bled to a cold trap for re-use. The residual mixture was hydrolyzed with ethanol, washed with 5% hydrochloric acid and then with sodium bicarbonate solution until neutral. The dried ether layer was distilled, perfluorostyrene being taken off at about 121°. After re-distillation the monomer was purified by passage through two preparative-scale chromatographic columns. Chromatographic analysis of the final product showed a small impurity peak on each side of the monomer peak. The areas of the two impurity peaks totalled less than 0.1% of the area of the monomer peak.

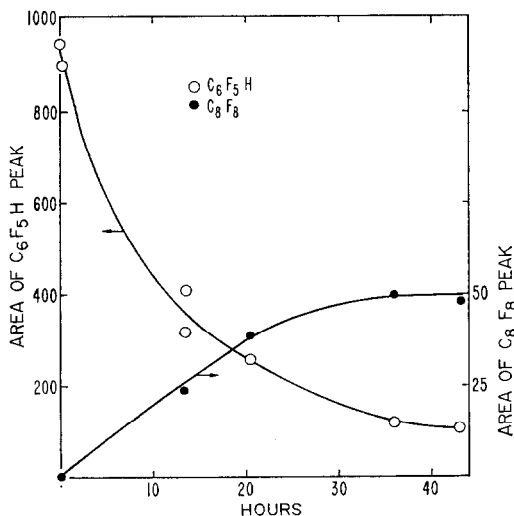


Fig. 1. Perfluorostyrene and pentafluorobenzene in hydrolyzed aliquot vs. reaction time at -20° before hydrolysis. Areas are in the same arbitrary units.

About 10 times more higher boiling material formed than perfluorostyrene. About one-third of the former was 2-*H* nonafluorobiphenyl. This is a known decomposition product of pentafluorophenyl-lithium⁸; presumably most of the residue was other decomposition products⁹. Perfluorostilbene was also identified in this material but the yield was small. No evidence of β -hydrononafluoroethylbenzene or of multiple addition of tetrafluoroethylene was found. Therefore, the low yield of perfluorostyrene is attributed to slowness of the reaction of pentafluorophenyl-lithium with tetrafluoroethylene compared with decomposition of the former.

Before committing the large quantities of material used in the above synthesis many variations were tried on a small scale in order to optimize conditions. Only a summary of these results follows. In each, the conditions not specified are those of the large scale runs and the yield is that of perfluorostyrene.

This yield was unaffected if pentafluorophenyl-lithium was made as above, by transfer with pentafluorophenyl iodide, or by direct metallation of this iodide in the presence of tetrafluoroethylene using excess lithium dispersion. Disadvantages of the second and third methods are formation of pentafluorotoluene in the second and the need to decompose the excess lithium in the third. Use of sodium instead of lithium dispersion gave a lower yield. The yield increased as the ratio of tetrafluoroethylene to pentafluorophenyl-lithium was increased from 3:1 to 6:1 to 15:1. However, at a ratio of 45:1 less perfluorostyrene formed than at a ratio of 15:1. After 120 h less perfluorostyrene remained than at 40 h. At -80° no perfluorostyrene could be detected in 24 h. Maximum yields were lower at 0° and at 25° than at -20° . Replacement of some ether by pentane or tetrahydrofuran gave lower yields.

A synthesis has been reported since this work commenced that might be more effective for a large scale effort¹⁰.

RESULTS

Physical transitions of perfluorostyrene

The initial experimental results on the polymerization process were quite erratic and uninterpretable until a phase study of the liquid monomer indicated the underlying reasons for the observed behavior.

Crystallization or melting is readily detected in our apparatus because the associated isobaric volume change manifests itself as a change in piston position with little change in applied force. A glass transition ideally would be marked by a change in slope of a piston position vs. force plot but in practice the high viscosity seems to obscure this by preventing equilibration of the sample. Additionally, although moderate superpressing of liquids is common, all other monomers in our experience crystallized instead of becoming glassy. Thus we had not previously studied a glass transition at high pressure.

Perfluorostyrene is very difficult to crystallize. When highly compressed it becomes viscous; the imposed pressure causes gradients that decay slowly enough to be observed. An example is in Figure 2 in which piston position is plotted vs.

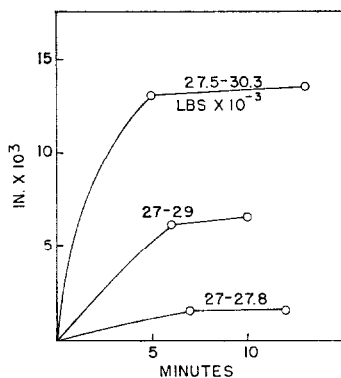


Fig. 2. Perfluorostyrene in the region of 10 000 atm, 22°. Characteristic behavior in the vicinity of the glassy state. Outward piston creep (in), after lowering load to the initial values shown on curves, as function of the time required for the system to equilibrate. At this time the load had risen to the final values indicated on curves.

time. The origin is taken as the piston position immediately after reduction of the force on the piston to 27 500 lb from a value several thousand pounds higher. With the hydraulic unit isolated from the pumping system the piston creeps out and the force builds up as shown on the upper curve. Two smaller force reductions gave less build-up as shown on the other curves.

Figure 3 is a plot of piston position as a function of force. The open and closed points were obtained as the force was applied and released respectively. The horizontal separation is due to packing friction. The effective force on the monomer, established by observing known pressure-induced crystallizations in our apparatus, is the arithmetic mean of the ascending and descending curves at any piston position. The dashed lines each connecting two of the same type of circles represent initial and final values after observations such as described for Figure 2. Below about 28 000 lb force the piston creeps about 10^{-3} in in a minute and then stops. Thus large-sized creep has a fairly sudden onset. Comparison of our observations with the stress decay rate in materials of known viscosity suggests that the viscosity of the monomer is about 10^7 poise when slightly into the region of large creep. Although not in the glassy range, this viscosity is about 10^9 times as great as at atmospheric pressure. An equation describing the effect of pressure on viscosity¹¹ reduces at very high pressure to a form in which the logarithm of the latter increases as $P/(f_0 - B_f P)$, where P is the pressure, B_f the compressibility of the free volume, and f_0 is the fractional free volume at a reference pressure. This would predict transition to glassy behavior as $B_f P$ approaches f_0 . The sudden

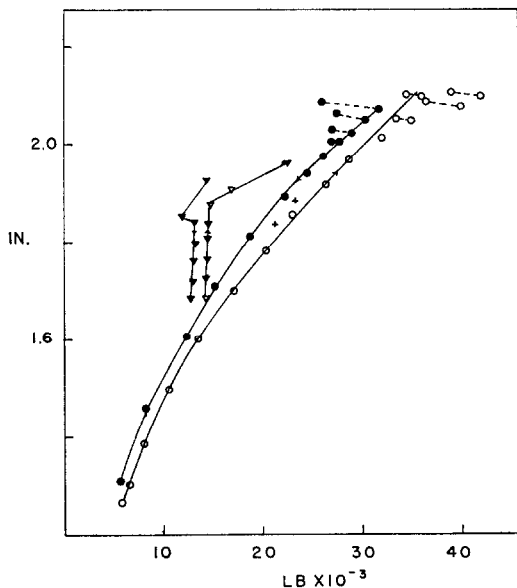


Fig. 3. Perfluorostyrene in the range of 2000 to 15 000 atm at 22°. Piston position as function of load. Dashed lines connect points where measurable creep occurred; See Fig. 2.

- | | | |
|-------------------|---|--|
| Liquid phase | { | ○ Pressure increasing. |
| | | ● Pressure decreasing. |
| Crystalline phase | { | ▽ Pressure increasing. |
| | | ▼ Pressure decreasing. |
| | | + Initial storage condition for producing crystallization. |

onset of considerable piston creep suggests that the viscosity is starting to rise rapidly. Therefore, we have taken the pressure at which the piston creeps 5×10^{-3} in in 5 min as the glass-transition pressure.

This transition is quite certainly not a crystallization because no piston creep at constant load occurs on decompression, even after days of storage under 40 000 lb load. In contrast, storage for 24 h with initial conditions indicated by the crosses gave a material which followed the filled triangles when decompressed. Re-compression after reaching the lowest triangle gave values indicated by the open triangles. This then locates the melting transition. Presumably under 40 000 lb load there was insufficient mobility to crystallize because the monomer was in the glassy state.

At higher temperatures the transitions occur at greater forces. Converting the observed forces to pressures, by dividing by the cross-sectional area of the cylinder bore, permits us to construct Figure 4 in which transition temperatures are plotted versus pressure. The freezing pressure is about half that of the glass transition.

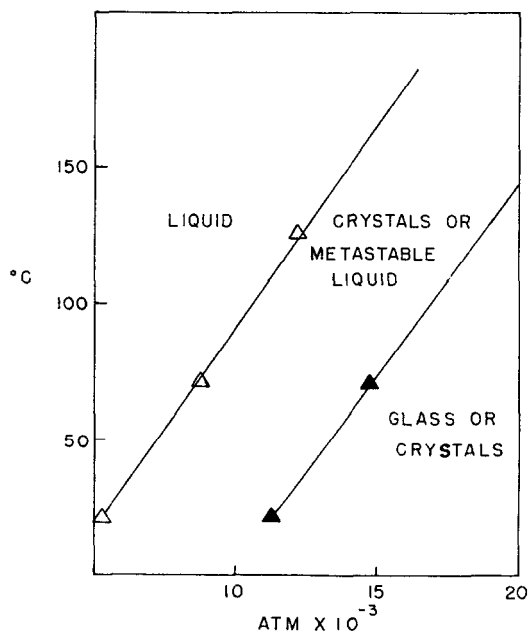


Fig. 4. Phases of perfluorostyrene. Δ Melting temperature at an indicated pressure. \blacktriangle Viscosity becomes high, near or approaching the glassy state.

Thermal polymerization

Polymer was found in the monomer recovered from the transition study. Since this sample had not been irradiated, an appreciable rate of thermal poly-

merization was indicated. Our chief effort has been devoted to the study of this thermal reaction.

The results obtained are listed in Table 1. Listed are the polymerization pressure, temperature, time and percentage conversion to polymer. The intrinsic viscosity of the polymer is included also, as is the polymerization rate, calculated as a first-order rate constant. These rates are rather irreproducible, since three experiments at 15 000 atm and 155° gave values differing by a factor of three. The cause of the difficulty is unknown. The last column in the Table indicates the physical state at the end of the run, as judged by reference to the lines in Figure 4 and by observation of piston displacement as the pressure was reduced. Symbols L, C, M and G indicate liquid, crystalline, metastable liquid and glassy states respectively. Crystallization apparently occurred only in long runs, and not always then. However, the presence of 10–20 per cent polymer causes the monomer to melt over a 1000–2000 atm pressure range and conceivably could make us miss the transition.

TABLE 1
THERMAL POLYMERIZATION OF PERFLUOROSTYRENE

Pressure (atm $\times 10^{-3}$)	Temp. (°C)	Time (h)	Conv. (%)	v_p (per cent h ⁻¹)	$[\eta]$ (dl g ⁻¹)	State ^a
20	155	0.25	36	170	0.18	M
20	125	1	28	32	0.20	G
20	97	1.7	2.0	1.2	0.30	G
20	97	3	2.3	0.8		G
15	155	1.9	43.6	30	0.15	L
15	155	0.83	12.3	15.7	0.14	L
15	155	3	27	10	0.18	L
15	138	1.0	7.8	8.1	0.16	M
15	123	1.5	10	7.0	0.29	M
15	97	4.3	7.5	1.8	0.37	M
15	92	5	6.9	1.4	0.33	M
15	65	117	8.7	0.078	0.27	G
15	17	68.7	0.02	0.0003		G
13.8	96	63.5	18.8	0.323	0.41	C
12.5	95	184	7.6	0.044	0.18	M
12.5	79	277	18.3	0.070	0.33	C
12.5	55	232	3.17	0.014	0.39	C
6.8	155	69	5.35	0.082	0.07	L
6.8	98	216	1.59	0.0074	0.11	L
6.8	55	210	0.084	0.0004		L

^a L, C, G and M signify liquid, crystalline, glassy and metastable liquid states, respectively.

Polymer did not form in an attempted thermal polymerization at autogenous pressure and 100° over two years duration. However, about 60 weight per cent of high-boiling material formed. Chromatographic analysis indicated that it contained

two components; their areas were in the ratio 1.2:1, in the order of their exit from the column. Separation of these, followed by examination on the mass spectrometer, indicated that both were dimers of perfluorostyrene. Their structures are unknown but presumably they are cyclic. Small amounts of both dimers were also detected in the polymerizations run at 15 000 and 20 000 atm at 155°. Approximate rates of formation of the total dimer fractions were 0.2 and 0.35 per cent h⁻¹ respectively. These values are negligible compared with polymerization rates under these conditions. No dimers were detected in monomer recovered from the run at 20 000 atm and 100°. Thus, it appears that dimerization increases only moderately with pressure but quite rapidly with temperature.

Radiation-induced polymerizations

Experiments were conducted at various dose rates at high temperatures and pressures. Results are listed in Table 2. Higher rates and lower intrinsic viscosities were found than in the corresponding thermal reaction. In the last two experiments glassy and crystalline solids were irradiated and then stored at high pressure out of the radiation field. Considerably more polymer formed in the former experiment. For this polymer the intrinsic viscosity was greater than in experiments without storage, despite the lower intensity in the latter. The overall rate is much greater than in the thermal polymerization. These results indicate that radiation creates long-lived propagating species in the glassy monomer.

TABLE 2

RADIATION-INDUCED POLYMERIZATION OF PERFLUOROSTYRENE

Pressure (atm × 10 ⁻³)	Temp. (°C)	Time (h)	Dose rate (rad h ⁻¹)	Conv. (%)	v_p (10 ³ per cent h ⁻¹)	$[\eta]$ (dl g ⁻¹)
15	17 ^a	141	1 200	0.74	5.2	0.15
15	65 ^a	65.6	1 200	8.11	129	0.24
15	17 ^a	2.4 ^b	150 000	5.43	45 ^e	0.23
15	17 ^c	3.2 ^d	150 000	0.065	0.39 ^e	

^a Irradiated as a glass.

^b In source. Stored 122 h.

^c Irradiated as a crystalline solid.

^d In source. Stored 166 h.

^e Based on total time.

Polymer properties

Preliminary experiments to evaluate the properties of the polymer have been performed, and the results are summarized here. The glass-transition temperature of the polymer is 194°¹². The rate of weight loss in vacuum at 310° is about 1 per cent min⁻¹. The polymer crosslinks inefficiently when exposed to radiation from ⁶⁰Co in vacuum at 45°. The ratio of scissions to crosslinked units, taken as the

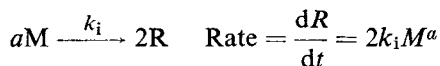
intercept of a plot of s , the sol fraction, plus $s^{1/2}$ vs. the reciprocal of the dose¹³, equals 1.3. The unirradiated polymer is soluble in perfluoroaromatics but not in perfluorinated ethers or alkanes.

DISCUSSION

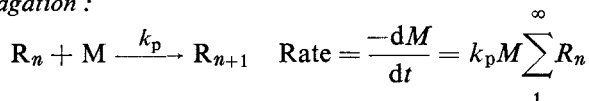
The presence of stiff phases gives difficulty in high-pressure work because such phases support stresses which result in pressure gradients through the sample. For the configurations used these might amount to 2000 atm in experiments in which the monomer had glassed or crystallized. Consequently, the effective polymerization pressures in such runs may be somewhat less than those listed.

The bulk-phase thermal polymerization of a monomer not subject to transfer would be expected to follow the radical mechanism:

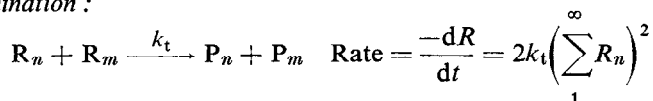
Initiation :



Propagation :



Termination :



Here M and R depict the concentrations of monomer and radicals, M and R respectively, P being the polymer formed during the reaction, k_i , k_p and k_t depict the rate constants for initiation, propagation and termination, respectively, a is the order of the initiation reaction and the letters m and n represent specific numbers of monomer units. Application of the steady-state approximation leads to equations for the polymerization rate, v_p , in per cent h^{-1} , and for the number average degree of polymerization, \overline{DP}_n . They are:

$$v_p = 100 \left(\frac{-dM}{Mdt} \right) = 100 \left(\frac{k_i M^a}{k_t} \right)^{1/2} k_p \quad (1)$$

$$\overline{DP}_n = \frac{k_p M^{\frac{2-a}{2}}}{2(k_i k_t)^{1/2}} \quad (2)$$

If combination instead of disproportionation occurs during termination, the right-hand side of equation (2) is twice as large.

In absolute rate theory, the activation volume and enthalpy determine the isothermal pressure dependence and isobaric temperature dependence of each rate, respectively. If the monomer compressibility is neglected, the dependence of

equations (1) and (2) is largely due to exponentials having the sums $0.5(\Delta_i - \Delta_t) + \Delta_p$ and $\Delta_p - 0.5(\Delta_i + \Delta_t)$ for v_p and \overline{DP}_n , respectively. Here each Δ is the activation term for the rate constant with the same subscript.

In highly viscous media diffusion may control propagation¹⁴. Different rate constants could be involved in the different phases. The metastable liquid region is regarded as liquid since the viscosity is not extremely high.

Figure 5 is an Arrhenius plot of the data recorded in Tables 1 and 2. In our preliminary work, the 15 000 atm isobar appeared to curve downward as the temperature increased¹⁵. This was interpreted as being due to depropagation becoming appreciable at 155° and 15 000 atm. Rates subsequently obtained under the same conditions are sufficiently high to make this seem unlikely. Furthermore, additional data at 6800 atm give a linear plot over the temperature range 55–155°, although polymer should be much less favored at the lower pressure.

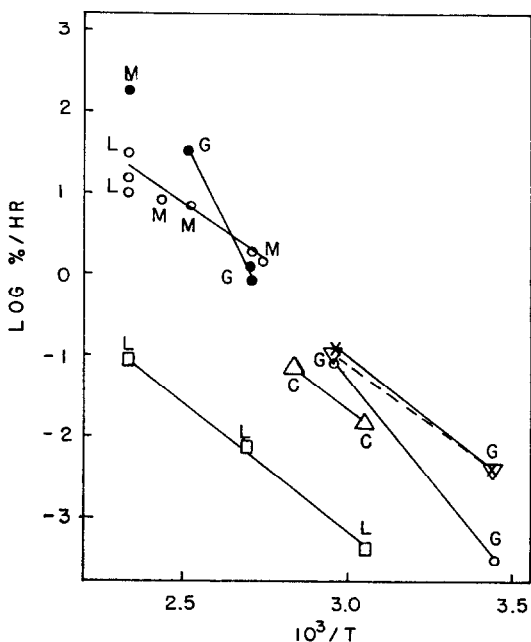


Fig. 5. Polymerization of perfluorostyrene, thermally initiated rates except as indicated: \square 6800 atm; \triangle 12 500 atm; \circ 15 000 atm; \times 15 000 atm, γ -ray; ∇ 15 000 atm, γ -ray corrected for thermal; \bullet 20 000 atm.

Letter associated with each point indicates phases of monomer at termination of polymerization: C = crystalline; M = metastable liquid; L = liquid; G = glass.

In the liquid phase, the activation enthalpies at 6800 and 15 000 atm are 15 ± 3 and 13 ± 6 kcal mole⁻¹, respectively*. The uncertainties given here and

* 1 kcal equals 4.184 kJ.

below assume that a rate, X , is uncertain by $0.5X$. This amounts to assuming a three-fold spread in possible values of each rate, as was found at 155° and 15 000 atm.

In the glassy phase at 15 000 and 20 000 atm, the activation enthalpies are 23 ± 4 and 40 ± 12 kcal mole $^{-1}$, respectively. In the crystalline phase at 12 500 atm, the value is 15 ± 10 kcal mole $^{-1}$. The high uncertainties in the last two enthalpies are due to the small temperature range of the data.

Rates in the presence of radiation are larger than the thermal rates. The dashed line in Figure 5 represents the hypothetical radiation-induced rate in the absence of a thermal rate. It was calculated as the square-root of the difference of the squares of the observed rates in the presence and absence of radiation. This would be valid for free-radical mechanisms in which the overall initiation rate equals the sum of the thermal and radiation-induced initiation rates and the termination rate is proportional to the square of the concentration of radicals. The activation enthalpy for this hypothetical rate is 13 ± 4 kcal mole $^{-1}$. This is the activation enthalpy for propagation minus half of that for termination, if the radiation-induced initiation rate is independent of temperature. Therefore, twice the difference between 23 and 13 is the activation enthalpy for thermal initiation at 15 000 atm in the glassy phase.

The pressure dependence of the rates at 155° and 95° is shown in Figure 6.

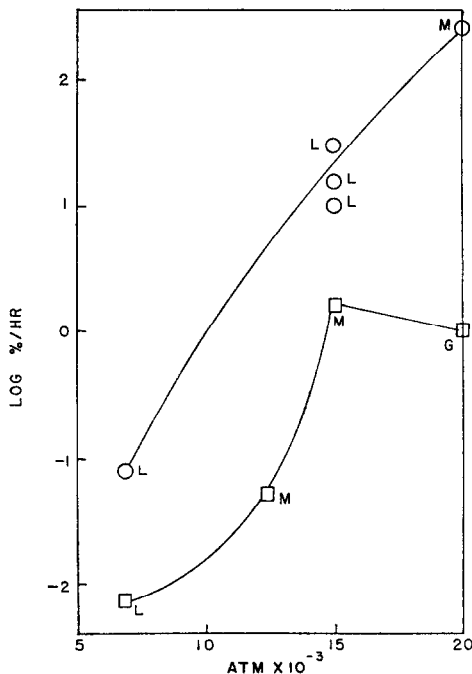


Fig. 6. Effect of pressure on the thermal polymerization rate of perfluorostyrene: ○ 155° , □ 95° .

The activation volume for the 155° isotherm is -20 ± 3 cc mole⁻¹. Commonly, propagation and termination steps combine to show an activation volume of -10 to -15 cc mole⁻¹. The more negative values here imply that the activation volume for initiation is negative. Consequently, the initiation is an associative process.

The isotherm at 100° has a maximum between 15 000 and 20 000 atm that presumably is due to the phase change from M to G. Below the maximum it is upward flexed. This is out of keeping with the usual finding and probably indicates that the intermediate rate is in error.

The dependence of the intrinsic viscosity, $[\eta]$, on the polymerization temperature and pressure is shown in Figure 7. The lines merely connect runs made at the same pressure. At constant pressure in either liquid, glass, or crystal, temperature increases resulted in decreased intrinsic viscosities. This is expected since thermal initiation commonly has a greater activation enthalpy than the rest of the mechanism. Glassy monomer formed polymer of lower intrinsic viscosity than would be obtained by extrapolation of the liquid-phase data. This may indicate diffusion control of propagation since initiation is unlikely to become diffusion controlled¹⁴. Termination is likely to be diffusion controlled in all our high-pressure runs¹⁶. Polymers formed in crystalline monomer have especially high intrinsic viscosities for the polymerization pressure.

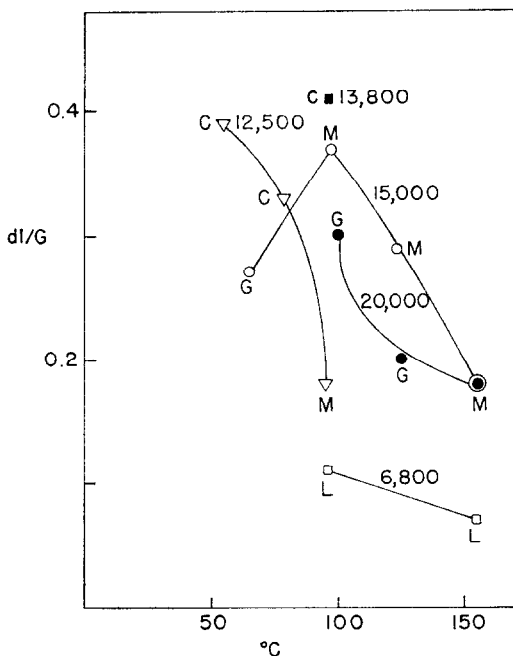


Fig. 7. Perfluorostyrene, intrinsic viscosity of polymer as a function of temperature of polymerization at different pressures. Letters near points indicate phase at termination of polymerization: □ 6800 atm; ▽ 12 500 atm; ■ 13 800 atm; ○ 15 000 atm; ● 20 000 atm.

ACKNOWLEDGEMENT

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Certain commercial materials are identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material identified is necessarily the best available for the purpose.

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