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Publisher *Taylor & Francis*

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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Garrett, R. R. , Hargreaves II, C. A. and Robinson, D. N.(1970) 'The Structurally Regular trans-1,4-Poly(chloroprene)', *Journal of Macromolecular Science, Part A*, 4: 8, 1679 — 1703

To link to this Article: DOI: 10.1080/00222337008059515

URL: <http://dx.doi.org/10.1080/00222337008059515>

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The Structurally Regular trans-1,4-Poly(chloroprene)

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SUMMARY

Radiation polymerization of large crystals of chloroprene formed within the temperature range -130 to -180°C has yielded the stereoregular trans-1,4-poly(2-chloro-1,3-butadiene). The monomer was found to have a glass transition temperature of ca. -180°C . Polymerization of monomer rapidly cooled to below -180°C was difficult and gave only structurally irregular polymer in low yield.

The stereoregular polymer has an equilibrium melting temperature T_m° of 105°C , about 25°C higher than that previously predicted for it. The new material was found to differ from other low-temperature polymerized neoprenes, especially in a head-to-tail content of at least 98% as opposed to ca. 90% for the high trans-content neoprenes heretofore available. The structurally regular polymer retained much of the ordered configuration of the crystalline monomer. Single crystals of this material were obtained from dilute solutions, the first reported for any poly(chloroprene). Recrystallization from more concentrated solution gave large and well-formed spherulites.

Apparent melting temperatures T_m^* of five known structural variants of

*Now employed by Pennwalt, Co., King of Prussia, Pennsylvania.

poly(chloroprene) plotted against the temperatures at which they were crystallized, T_c , followed Mandelkern's relationship with a slope of $\frac{1}{2}$. The T_m° obtained by extrapolating these data for the stereoregular polymer agreed well with the dilatometric T_m° . Glass transition temperatures T_g were well represented over the entire composition range by Gordon and Taylor's equation with $K = 1$.

Electron micrographs of the as-polymerized stereoregular polymer and of single crystals of trans-poly(chloroprene) are presented.

INTRODUCTION

We report the preparation and characterization of the stereoregular trans-1,4-poly(chloroprene) having at least 98% head-to-tail structure. The material is a white, crystalline solid having an asbestoslike appearance in that it is easily separated along cleavage surfaces parallel to the long axes of the original monomer crystals. Molecular weights of the order of 10^5 were obtained, and this material was completely soluble in solvents having solubility parameters of about 9, such as benzene. The stereoregular polymer had an equilibrium melting temperature T_m° of 105°C and a glass transition temperature T_g of -45°C . Above its melting point it could readily be molded to give tough slabs which, from density measurements, had a degree of crystallinity of about 60%.

From the early data of Maynard and Mochel [1], Flory extrapolated a value of $T_m^\circ = 80^\circ\text{C}$ for the "hypothetical pure trans polymer" [2]. The latter author based his calculations on the assumption that the original data were obtained on material comprising 97% trans 1,4 units "doubtless in head-to-tail arrangement" [2, p. 244]. It appears that, for this particular system, the foregoing assumption is not correct. It is primarily this structural aspect that is elucidated in the present work.

Many literature references exist that deal with the preparation of stereoregular poly(butadiene) by using transition metal complexes as well as cationic and organometallic initiators. Efforts in this laboratory to carry out similar preparations with chloroprene have been uniformly unsuccessful. Various high trans content polychloroprenes have, however, been prepared, although none of these has proved to be stereoregular. The preparative method generally employed to achieve improved structural regularity has been polymerization at low temperatures. Thus, Maynard and Mochel showed as early as 1954 that the melting point of the crystalline phase of

these polymers is an inverse linear function of the polymerization temperature [1], and they concluded that chloroprene polymerized at -50°C gave a substantially 100% *trans*-1,4 product. These authors, however, had no method for estimating the head-to-tail content.

In 1965, Gent [3] reported rates of crystallization and melting points for Neoprene HC (a product of E. I. du Pont de Nemours and Co.), a material he referred to as *trans*-polychloroprene. Gent noted evidence of deviations from a regular structure as indicated by an abnormally low index n in the Avrami relation which resulted from a marked retardation of the later stages of crystallization. This evidence indicates the presence of noncrystallizing groups, as Mandelkern has shown [4]. The melting temperature which Gent observed for his highest *trans*-content polymer was 69.5°C . Our data suggest that such a sample would have a *trans*-content of 90-95% and a head-to-tail content of about 90%, i.e., a total of 15 to 20% structural irregularities.

After describing the preparation, we present the T_m^* vs. T_c relationship for stereoregular *trans*-1,4-poly(chloroprene) in the first section and then compare some of its properties with those of neoprenes having known amounts of structural irregularities. We show that these irregularities suffice to account for the equilibrium melting points we found for the less regular polychloroprenes. Finally, we wish to present an initial and incomplete microscopic examination of crystalline forms of the stereoregular polymer.

PREPARATION AND PROPERTIES OF STEREOREGULAR *trans*-1,4-POLY(CHLOROPRENE)

Experimental

Initial radiation polymerizations of chloroprene in liquid nitrogen at -196°C always gave a high *cis* content (12-15%) polymer [5]. We found that chloroprene has a T_g near -180°C^* and that radiation polymerization of monomer crystallized above T_g is necessary to provide the stereoregular polymer. Several crystallization methods were tried successfully; the following appeared to be the most convenient:

*Originally found using the forerunner of the Du Pont Thermo-mechanical Analyzer [7] and later confirmed by DTA.

Polymerization-grade chloroprene (25 to 50 ml) was charged to a ½-in. diam, stoppered Pyrex test tube which had been either drawn to a sharp point at the bottom or was provided with a ½-mm capillary twisted helically so as to induce an advancing crystal front of narrow dimensions on cooling (crystallization method of Bridgman [6]). No effort was made to exclude traces of moisture or air. The test tube was lowered at the rate of 1 in./hr, first into an air space held near the melting point T_m of the monomer (-130°C), and then into a liquid bath held at $10\text{--}25^\circ\text{C}$ below T_m . The narrow crystallizing front gave rise to elongated, coarse crystals, evidently very different from the clear, brittle glass which forms when the monomer is cooled directly in liquid nitrogen. Rapid cooling to -155°C gave a polycrystalline texture which was also easily differentiable from the slowly crystallized materials and which gave much lower polymer yields than did the latter on irradiation.

Although it was possible to obtain some yield (2-3%) of the stereoregular polymer by irradiation in an electron beam (2.5 MeV, total dose 10 to 100 Mrads), temperature control was difficult, and the low penetration of the beam led to the formation of a skin of polymer surrounding unpolymerized monomer crystals. X rays were preferred, and a van de Graaff accelerator, equipped with a gold target, was employed which generated a 3 MeV electron beam. The crystalline monomer was irradiated at a dose rate of 40,000 to 60,000 rads/min at temperatures ranging between ca. -135 and -196°C . The variation in yield over this temperature range appeared to be small. Total doses of 1 to 4 Mrads resulted in yields of monomer-free stereoregular polymer varying between 10 and 20%.

It even proved possible to use a 45 kV X ray unit to obtain stereoregular material, though in minute amounts. A 40-g sample, crystallized as described above, was irradiated at a distance of 8 in. from the source (the beam traveling only through air) for 25 min at -196°C . Five milligrams of product resulted.

Irradiated tubes were permitted to warm to room temperature rapidly. Absence of a posteffect was established by several experiments in which irradiated samples were warmed slowly to room temperature. Increased yields did not result.

Solid polymer was separated from unreacted monomer and was washed repeatedly in methanol, the last wash comprising a soaking for 7 days with repeated changes of methanol. The last traces of methanol were removed in vacuo at room temperature.

Radiation polymerization of liquid chloroprene in the temperature

range -78 to -130°C proved difficult. No product was obtainable by X ray, though a soft rubber smelling strongly of chloroprene dimer was obtained in low yield from an electron beam after a total dose of 2×10^8 rads had been absorbed from a resonant transformer (2.5 MeV, 0.5 mA, total exposure time 13 min). Temperature control was attempted by irradiating (in short bursts) a film of liquid monomer less than 2 mm thick which was in intimate contact with coolant.

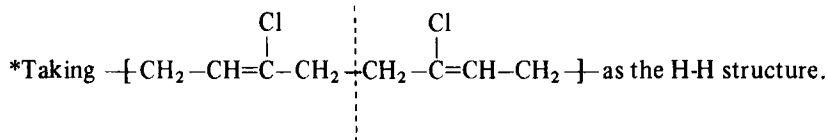
Polymerization of glassy monomer was attended with similar difficulties. It was not possible to determine the total dosage with great accuracy because the electron beam irradiation was carried out under a layer of liquid nitrogen which varied somewhat in thickness during the course of the experiment, and some electron absorption occurred in this blanketing layer. A series of short exposures of the order of 1 min were used to build up a total absorbed dose to an estimated 10^8 to 10^9 rads. The glassy chloroprene film was about 1 mm thick. Care was taken to exclude oxygen in order to avoid ozone explosions. Unreacted monomer was removed from the rubbers by the method described above.

In one experiment traces of water were excluded: A 25-g sample of polymerization-grade chloroprene was redistilled into a flamed-out Pyrex tube, degassed by alternate freezing and thawing under vacuum below -100°C , sealed, and crystallized at -150°C as described previously. It was given a total dose of 2 Mrad in the electron beam of a 2-MeV resonant transformer in a bath held at -150°C . A low (5%) yield of soluble, stereoregular polymer resulted.

Microstructure Determination

Ten per cent solutions of the polymers in Matheson-Coleman and Bell spectroscopic grade CHCl_3 were prepared for NMR and IR measurements.

Nuclear Magnetic Resonance Spectroscopy. The 220 MHz PMR spectra of the foregoing solution at 50°C were run on a Varian HR-220 spectrometer. The internal reference was tetramethylsilane. Relative concentrations of head-to-tail (H-T), head-to-head* (H-H), and tail-to-tail (T-T) sequences were determined by planimeter area measurement of the corresponding methylene group resonances at 2.40, 2.54, and 2.25 δ , respectively [8-10]. The estimated standard deviation was 0.5%. The H-H and T-T areas were



equal within experimental error. The olefinic resonance at 5.46δ was partially resolved into the expected triplet. No cis-olefinic resonance was detected in the stereoregular trans-1,4-poly(chloroprene).

Infrared Spectroscopy. A Perkin-Elmer Model 221 infrared spectrophotometer equipped with a prism-grating interchange was used to obtain spectra covering the range 0.6 to 25μ ($16,667$ - 400 cm^{-1}). The trans-1,4, cis-1,4, 1,2-, and 3,4-polymerization isomers were determined from absorbance measurements at 1660.3 , 1652.2 , 925 , and 883 cm^{-1} , respectively. The calibration data and method of Ferguson [11, 12] were employed.

Transition Temperature Determinations

The dilatometric procedures adopted here for determining T_m° have been described elsewhere [13], as have the general techniques of transmission depolarization [14] used to obtain T_m^* with a hot-stage microscope. The heating rates used in the present work for hot-stage microscopy were faster than those previously employed, however, in order to assure that negligible recrystallization occurred during the T_m^* determination. The Köfler micro hot stage was calibrated according to the manufacturer's instructions at the heating rates actually followed. These rates are specified in the Results and Discussion Section. The standard deviation of a single measurement was $\pm 1.0^{\circ}\text{C}$.

The use of thin microscope samples (not exceeding a few mils in thickness) proved critical in assuring that crystallization actually occurred at T_c . This subject is discussed in the next Section. Films were annealed above T_m° on a cover glass and were transferred within less than 1 sec to the hot stage which had previously been stabilized at $T = T_c$. The use of thicker samples gave spuriously high values of T_m^* as did the use of heating rates much slower than those specified. All measurements were made with cover glass and shielding.

Glass transition temperatures were measured with a device [7] that was the forerunner of the Du Pont Thermomechanical Analyzer (TMA), differing from it slightly in construction but being similar in principle and method of operation. Many of these data were confirmed by length-temperature measurements for which an instrument similar to that of Dannis [15] was used. A Du Pont 900 Differential Thermal Analyzer was chosen for the DTA experiments.

Preparation of Single Crystals

Attempts to produce single crystals of the stereoregular polymer from

dilute solutions in good solvents did not succeed. Crystallization from a poor solvent, a mixture of 100 g ethyl acetate and 40 g hexane, was carried out as follows: 0.200 g of stereoregular polymer was almost completely dissolved in the foregoing mixture at 50°C. Minor amounts of insolubles were removed by filtration at 50°C. Cloudiness developed on cooling to 0°C but disappeared after slow warming to 30°C (the minimum dissolution temperature was not exceeded by more than 1-2°C). The sample, slowly cooled to 25°C, was allowed to stand at room temperature for several days before electron microscopy was attempted. The settled dispersion was applied to a carbon substrate and was shadowed with platinum. An RCA EMU 3G electron microscope was used at 10,000X and 50,000X. The scanning electron microscope employed for the as-polymerized samples was a Stereoscan model manufactured by the Cambridge Instrument Company.

RESULTS AND DISCUSSION

Repeated experiments showed that monomer quenched rapidly in liquid nitrogen produced either minor amounts (<1%) or no polymer when irradiated under the same conditions as those used for the successful preparation described in the Experimental Section for crystallized monomer. The same batch of monomer was used as a source in both cases. This behavior became clear when a T_g of -180°C was found for chloroprene on the TMA [7], and it was shown that crystal formation occurred only in the range -140 to -180°C. Slow crystallization, with correspondingly larger crystals, gave a substantial increase in yield, i.e., from 5% to about 20%. Other systems are known for which irradiation of larger crystals gives a greater limiting conversion than do fine crystals [16]. No "posteffect" was observed.

Although a detailed study was not made, our experiments suggest that the presence of traces of water does not lower, and may indeed raise, the limiting conversion. Such behavior has also been reported for other systems [17]. We did find, however, that the scrupulous exclusion of water does not prevent polymerization completely.

In general, yields were found to increase with total dose up to a limiting conversion of ca. 20%, but a quantitative establishment of this relationship was not attempted because of the marked dependence of yield on polycrystalline texture (i.e., the size and number of crystallites) of the monomer. The latter variable was found difficult to control accurately.

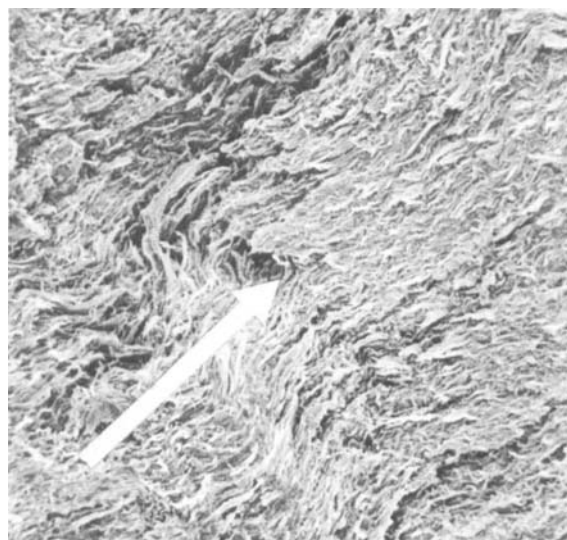
Polymerization was observed to occur substantially unhindered in the presence either of inhibitors of ionic polymerizations such as acetone, or of free-radical inhibitors such as hydroquinone. Such materials probably crystallize separately from the chloroprene, and it was concluded that these experiments reflect the difficulty of introducing reagents to the site at which the solid-state polymerization actually occurs rather than cast light on the mechanism of the reaction.

Stereoscan microscopy on the as-polymerized polymer (Figs. 1-3) suggested a fibrous structure, the grain of which retained the texture of the original monomer crystals. In fact, under low magnification the appearance of the crystallized monomer was substantially unaltered by the polymerization process. The arrow in Fig. 1 indicates the direction of the original elongated monomer crystals.

This behavior is not unique. Other solid-state polymerizations are known in which the products show a structure and orientation directly related to the host lattice [17, 18]. These have been called "lattice controlled" or "topotactic" polymerizations. Nevertheless, the way in which the crystal lattice dictates polymer structure is not an area of universal agreement. The site at which the polymerization reaction takes place, for example, is often not clear.

In addition to lattice-controlled polymerizations, solid-state polymerizations are also known [19, 20] that are generally believed to initiate at surfaces or defects in the structure of the solid monomers. Such reactions generally yield structurally irregular products. It seems reasonable to suppose that the factor that determines which of the foregoing mechanisms controls a given solid-state polymerization is related to the positioning and lattice constraints of the monomer units. If these units are unfavorably disposed and held, polymerization, if it takes place at all, should indeed occur only at defect sites or at surfaces where sufficient free volume for necessary reordering is available. In that case lattice constraints would not appear to be importantly involved in the polymerization process. We believe the polymerization of glassy chloroprene to be of this type.

In an ideally topotactic process, however, the structure of the polymer should be controlled by constraints peculiar to the monomer crystal lattice. The low entropy state prevailing after completion of monomer crystallization should be largely retained after polymerization. In these cases polymerization and polymer crystallization may be concomitant, and the formation of a structurally regular product should ensue. In par-



↔
200 μ

Fig. 1. Stereoscan electron micrographs of native stereoregular polymer.

ticularly favorable cases polymerization could involve only a redistribution of electrons. The volume change on polymerization would then be expected to be small, and the reaction rate should be virtually temperature-independent. More likely, however, is that a slight change of position during the polymerization reaction will be required in order to fit monomer units into the polymer crystal lattice. If this motion includes a twisting about one of the axes of the original monomer lattice, it seems reasonable to suppose that such twisting may be additive, and that as polymerization proceeds, the ultimate unit on the new polymer chain may become sufficiently turned so that it is no longer favorably disposed to accept another monomer unit from the host lattice. Such considerations could account for the observed limitations on yield of stereoregular poly(chloroprene) since the proposed defect production mechanism should effectively terminate the chain. Tensile stresses caused by the volume decrease on polymerization may also ultimately stop the polymerization by causing extensive fracturing [21]. Mechanisms such as these might be expected to give rise to some limiting value of the yield.





 40 μ

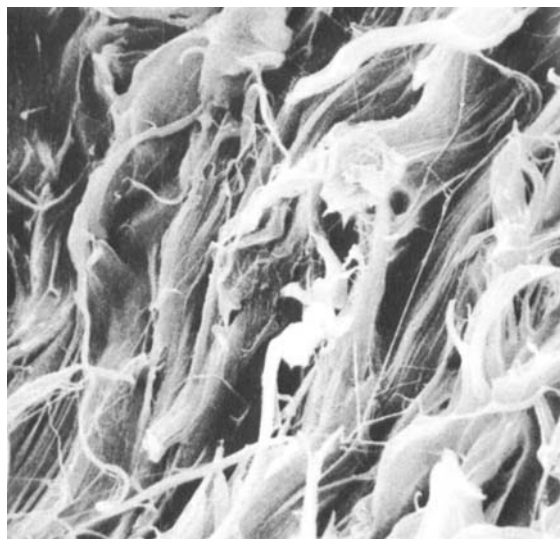
Fig. 2. Stereoscan electron micrographs of native stereoregular polymer.

A direct relationship between the monomer and polymer crystalline lattices has been found in other systems [22]. We believe this relationship exists in the case of polymerization of crystalline chloroprene. Our belief is based largely on the retention of the shape of the monomer crystals even after polymerization: the fibrouslike structure shown in Figs. 1-3 was oriented generally along the same direction as that of the original elongated monomer crystals, i.e., approximately perpendicular to the advancing crystalline front. The surface shown in Figs. 1-3 was distorted somewhat by monomer removal, but the effect was clearly visible when the monomer-swollen material was examined.

Finally, we have no reason to believe that polymerization initiates only at pre-existing defect sites. The poor yield resulting from the irradiation of many small crystals of chloroprene would, in fact, argue against such a conclusion.

Melting and Recrystallization

The well-ordered crystalline lattice formed during polymerization of crystalline chloroprene is never completely recovered on recrystallization,





 10 μ

Fig. 3. Stereoscan electron micrographs of native stereoregular polymer.

presumably due to the adverse influence of molecular entanglements. A dilatometric determination of the initial melting temperature at a heating rate of 1°C/day near T_m^o gave an equilibrium melting temperature of 105°C for the stereoregular polymer. Extrapolated values from T_m^* vs. T_c data also yield $T_m^o = 105^\circ\text{C}$ with an estimated error of $\pm 2^\circ\text{C}$ as shown in Fig. 4. Heating rates are given in Table 1. These rates are slow enough to assure reasonably accurate thermal measurement ($\pm 1^\circ\text{C}$) but rapid enough to preclude appreciable annealing at temperatures between T_c and T_m^* .

Except for the last entry, each value in Table 1 represents the mean of five determinations. The melting point of the +40°C polymer is more difficult to obtain by this method, however, because of poorly developed crystallinity, and we took the mean of ten determinations carried out on different portions of the same sample.

It is evident (Fig. 4) that these data stand in good accord with those of Maynard and Mochel [1] except in the case of their most highly crystalline sample, B. For that sample their dilatometer indicated a very low slope below $T_c = 50^\circ\text{C}$. At temperatures below 50°C, however, this

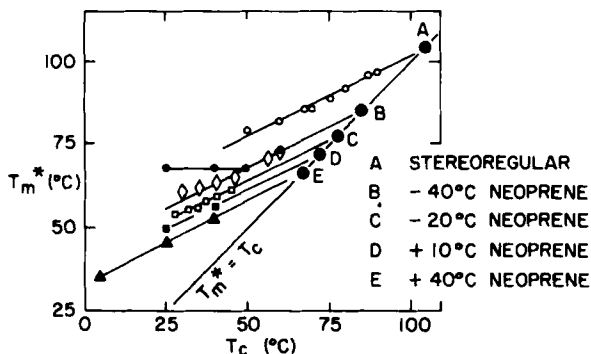


Fig. 4. Apparent melting temperatures T_m^* of neoprenes of varying structural regularity plotted against the temperatures at which they were crystallized T_c . (A) Stereregular polymer, present work. (B) Neoprene polymerized at -40°C by Maynard and Mochel [2]: (●) Maynard and Mochel's data [2]; (◇) present work. (C) Neoprene polymerized at -20°C . (D) Maynard and Mochel's data for neoprene polymerized at $+10^\circ\text{C}$ [2]. (E) Neoprene polymerized at $+40^\circ\text{C}$: (▲) data of Maynard and Mochel [2]; (△) present work.

material crystallizes in a matter of minutes, and it is likely that the center of their dilatometric sample underwent detectable crystallization at $T_c \approx 50^\circ\text{C}$ as the mass of packed films that Maynard and Mochel used was cooled to the temperatures of the various crystallizing baths set below 50°C , leading to spuriously low slopes. We observed such an effect when we used samples thicker than a few tenths of a millimeter. Even the thin samples we employed showed a slight upwards curvature for the readily crystallizable materials at lower temperatures (Fig. 4). Dilatometry does not appear to be the method of choice for obtaining the T_m^* vs. T_c relationships for readily crystallizable polymers. Similar discrepancies have also arisen in the recent literature: see Note Added in Proof, p. 1703).

Density measurements indicated that the stereoregular trans-poly(chloroprene) crystallized more rapidly and to a higher degree than did the previously available polychloroprenes. Bunn's value of 1.33 g/cc for the density of the crystalline phase [23] was used to show that 60% crystallinity was achieved in a few minutes at 25°C . This rate contrasts with those for uncured Neoprene HC, a low temperature polymer, which develops about 25% crystallinity in 2 days at 25°C ; Neoprenes AC and AD, about 20% in a few days at 25°C ; Neoprenes W and GN, 8-12% in one month at 25°C ; and Neoprenes GRT and WRT which, as vulcanizates, develop 5-10% crystallinity in 1 month and 3 months at 0°C , respectively.

Table 1. T_m^* and T_c Data for Various Polychloroprenes and Equilibrium Melting Temperatures Obtained by Linear Extrapolation

T_m^o (°C)	T_c (°C)	T_m^* (°C)	Annealing time	Heating rate (deg/min)
<u>Stereoregular Polymer</u>				
105	90	97	3 weeks	4
	87	96	24 hr	4
	80	92	8 hr	4
	76	89	30 min	4
	70	86	10 min	4
	68	86	5 min	5
	60	82	2 min	20°/3 min
	50	79	1 min	20°/3 min
<u>Polychloroprene Polymerized at -40°C [2]</u>				
84	60	73	10 days	4
	56	70	10 days	4
	46	66	1 hr	5
	40	63	15 min	7
	35	62	10 min	7
	30	60	10 min	7
	<u>Polychloroprene Polymerized at -20°C</u>			
77	45	62	10 days	4
	40	59	6 days	4
	37	58	4 days	4
	35	55	2 days	5
	32	55	1 day	6
	28	54	1 day	7
<u>Polychloroprene Polymerized at +40°C</u>				
67	40	53.5	4 weeks	4

The molecular weight of the stereoregular polymer appeared to be high. An osmometric determination was not carried out, but one sample which was 100% soluble had an inherent viscosity of 1.29 dl/g in benzene at 30°C, measured at a concentration of 0.1 g/100 ml solvent. This compares with a typical value of 1.3 dl/g for standard free radical emulsion polymerized poly(chloroprene) which corresponds to a viscosity average molecular weight of 300,000 g/mole.

Except for slight deviations at low temperatures, the data of Fig. 4 are well represented by straight lines with a slope of 0.5. The relation

$$T_m^* = \frac{1}{2}(T_m^{\circ} + T_c) \quad (1)$$

was first adduced by Lauritzen and Hoffman [24] for crystallization from dilute solution and later by Mandelkern [25] for crystallization in bulk polymers. Gopalan and Mandelkern [26] have more recently shown that Eq. (1) is a special case of the general relationship

$$T_m^* = \left(\frac{a}{2n}\right)T_c + T_m^{\circ} \left(1 - \frac{a}{2n}\right) \quad (2)$$

where a is the ratio of the interfacial free energy of a chain emerging from the 001 interface of a mature crystal to that of a chain similarly emerging from a nucleus of critical size, and n is the ratio of the thickness in the chain direction of the mature crystal to that of the nucleus. There is no size restriction in lateral directions. Equation (2) reduces to Eq. (1) when $a = n = 1$. For the extrapolation to be valid, the quantities a and n must be independent of T_c over the entire range and the molecular weight must be high. The data of Fig. 4 suggest that the foregoing simplifying relationships are justified in this case.

Gopalan and Mandelkern warn that the extrapolation of T_m° from the linear relationship between T_m^* and T_c is justified only if determinations are carried out on samples having a low degree of crystallinity. Unless the degree of crystallinity is prevented from becoming too high, spuriously low slopes are observed. This warning accords with our experience, and the annealing times which we report correspond to the times required for crystallinity to develop only to an extent clearly detectable between crossed polars at each T_c under the prescribed conditions. Gopalan and Mandelkern point out that this extrapolation procedure also requires that T_m^* be determined in such a manner that there be no change in crystallite size subsequent to crystallization, an important consideration which we have emphasized in the previous Section.

The data of Table 1 are extrapolated in Fig. 4 beyond the experimentally accessible region to the intersection of the line $T_m^* = T_c$, yielding the equilibrium melting points T_m^0 listed in Table 1. The theoretical basis for this procedure has been discussed in detail by Mandelkern [25, 26] and has been established for a variety of polymers.

A value of $T_m^0 = 105^\circ\text{C}$ was obtained in this way for the stereoregular polymer. For the same material $T_m^0 = 105 \pm 3^\circ\text{C}$ was also found dilatometrically.

The melting temperature listed in Table 1 for poly(chloroprene) polymerized at -20°C provides experimental support for the treatment chosen by Gent [3] to account for the recrystallization behavior of this polymer as a function of T_m^0 . Although the melting point which Gent actually observed for this polymer was about 20°C lower, it was necessary for him to assume $T_m^0 \approx 80^\circ\text{C}$ in order to obtain agreement with his theoretical analysis (Gent's Fig. 11 in Ref. 3). Our value of T_m^0 of 77°C (Table 1) for this material is therefore in good agreement with the value required by Gent's analysis.

The complete molecular structure of the stereoregular polymer has not been elucidated by X-ray diffraction for lack of sufficiently oriented specimens. Monomer removal unfortunately causes sufficient distortion of the fiber orientation so that good fiber patterns are not readily attainable. Powder diagrams of finely divided but unmelted stereoregular polymer proved to be at least qualitatively similar to those of other high trans-content polychloroprenes prepared at low temperatures by free radical catalysis. Stereoregular polymer appears to have the same unit cell as that reported by Bunn [23] for other crystalline polychloroprenes. We have no evidence for the existence of more than one crystalline phase in poly-(chloroprene) unlike the case of trans-1,4-poly(isoprene) for which two crystalline forms are well known [27]. No evidence of a solid-solid transition was detected in this work, at least within the temperature range $+25$ to $+105^\circ\text{C}$.

Double endotherms were, however, sometimes seen in thermograms of stereoregular polymer that had either been subjected to mild heat treatment (insufficient for complete melting) or that had been prepared by methods other than the preferred one, namely high energy X-ray polymerization of the crystalline monomer. The small amount of stereoregular polymer resulting from irradiation of crystalline monomer with a 45 kV X-ray unit yielded the thermogram shown in Fig. 5.

Second and successive meltings of the same material showed the disappearance of the 105 to 110°C peak, a single lower peak being observed

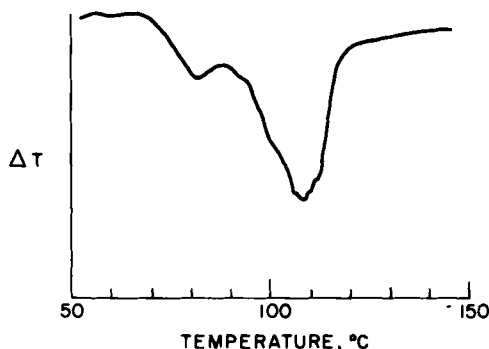


Fig. 5. Thermogram of the initial melting of stereoregular polymer polymerized in a 40-kV X-ray unit.

in the temperature range $50^{\circ}\text{C} < T_m^* < 95^{\circ}\text{C}$ depending upon the crystallization temperature.

We believe that unmelted, as-polymerized stereoregular polymer exists in the form of extended-chain or bundle crystals, but that lower melting folded-chain crystals form after initial melting and recrystallization has occurred. The lower peak in Fig. 5 may possibly have been due to a low molecular weight fraction having a short extended-chain form. The matter has been discussed by Bell and Dumbleton with regard to other systems [28].

Structural Configuration

Infrared and 220 MHz PMR spectral data (Fig. 6) were used to establish the structure of the stereoregular polymer. These data are compared in Table 2 and in Figs. 6 and 7 with those for three other polychloroprenes.

The data of Table 2 disagree somewhat with those previously reported for free radical polychloroprenes by Maynard and Mochel [29], but these small disparities can be attributed to the improved analytical methods presently available [8-12]. The product obtained by electron beam irradiation of liquid chloroprene had an anomalously high degree of structural irregularity. This may be due at least partly to the difficulty of controlling the polymerization temperature.

The influence of polymerization temperature on trans-1,4 content of free radical-polymerized poly(chloroprene) is shown in Fig. 8. The points shown at 40, 60, 80, and 85°C are averages of three determinations. The

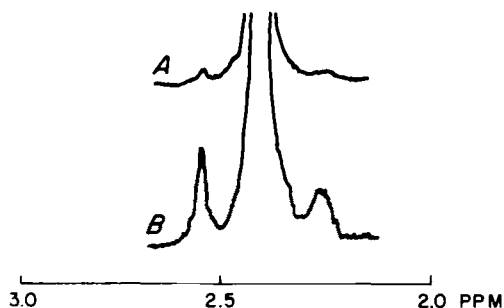


Fig. 6. 220 MHz PMR spectra. (A) Stereoregular polymer $\eta_{inh}^{30^\circ C} = 1.26$, concn. 0.1 g/dl solv. (B) A high molecular weight fraction of poly(chloroprene) polymerized at $+40^\circ C$.

Table 2. NMR and IR Analyses of Polychloroprenes

Sample preparation	Polymeri- zation temp. ($^\circ C$)	NMR % H-T	IR		
			% cis	% 1, 2	% 3, 4
Irradiation of crystalline monomer	-150	97.8	0	0	<0.5
Irradiation of liquid monomer	-130	81.6	7	0.3	9.7
Free radical poly- (chloroprene)	- 20	91.5	6	0.7	0.5
Free radical poly- (chloroprene)	+40	88.9	13	0.9	0.3

data support Maynard and Mochel's belief [1] that the product made at $-50^\circ C$ approaches 100% *trans*-1,4, but this does not appear to be true for the H-T sequence isomerism in liquid systems.

Few literature data exist for the H-T sequence analysis in poly(chloroprene). Ferguson [11] gave a range of 70-80% H-T, but this estimate was based on 60 and 100 MHz spectra and is somewhat low when compared with the more accurate 220 MHz data of Table 2. The sample referred to by Ferguson [11] as "*trans*-poly(chloroprene)" was not the stereoregular

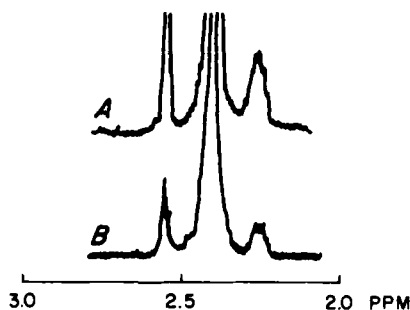


Fig. 7. 22 MHz PMR spectra. (A) Product from irradiation of liquid chloroprene at -130°C . (B) Poly(chloroprene) polymerized at -20°C .

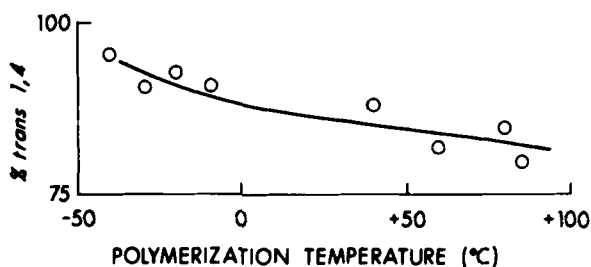


Fig. 8. *trans*-1,4 Content of polychloroprenes prepared by free radical catalysis at various temperatures.

polymer of the present work but rather the free radical product prepared by Maynard and Mochel at -40°C . This accounts for the low (83%) H-T content Ferguson found [12, 30] for this sample from 60 MHz spectra.

Melting Point Depression

The structural irregularities listed in Table 2 for polychloroprenes polymerized at -20 and $+40^{\circ}\text{C}$ permit calculation of their depressed melting points and comparison with the observed values reported in Table 1. The pertinent relationship is [31]:

$$\ln N_2 = \frac{-\Delta H_u}{R} \left(\frac{1}{T_m} - \frac{1}{T_m^0} \right) \quad (3)$$

where N_2 is the mole fraction of the crystallizing component; R , the gas constant; ΔH_u , the molar heat of fusion of *trans*-1,4-poly(chloroprene); and T_m the melting point depressed by the presence of $(1 - N_2)$ mole fraction of randomly distributed structural irregularities.

With ΔH_u taken to be 1890 cal/mole, the expected melting points of polychloroprenes polymerized at -20 and $+40^\circ\text{C}$ calculated according to Eq. (3) from their known structural irregularities listed in Table 2 are found to be 81 and 66°C , respectively, in good agreement with the measured values (Table 1) of 77 and 67°C .

The heat of fusion used in Eq. (3) was obtained by recalculating the data of Maynard and Mochel [1]. These authors calculated ΔH_u from the simplified relation appropriate for an ideal solution [31]:

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{R}{\Delta H_u} \left(\frac{V_2}{V_1} \right) v_1 \quad (4)$$

although their data permitted the application of the more general relationship [31]:

$$\frac{\frac{1}{T_m} - \frac{1}{T_m^0}}{v_1} = \frac{R}{\Delta H_u} \left(\frac{V_2}{V_1} \right) (1 - \chi_1 v_1) \quad (5)$$

where v_1 is the volume fraction of diluent; V_2 and V_1 the molar volumes of polymer and diluent, respectively; and χ_1 is the polymer-solvent interaction parameter. Using Maynard and Mochel's data we find the appropriate value for the heat of fusion of trans-poly(chloroprene) to be 1890 cal/mole (instead of their reported value of 2010 cal/mole) and the value of χ_1 for the neoprene-xylene system to be 0.43. The latter value is in excellent agreement with values for χ_1 of 0.42-0.44 determined independently by equilibrium swelling measurements by Souffie [32] in a variety of aromatic solvents such as toluene. The above value for ΔH_u is supported at least to some degree by a calorimetric determination which yielded 1400 cal/mole for the heat of fusion of a sample of previously unmelted (but monomer-free) stereoregular polymer. From the calculated value of 1890 cal/mole the calorimetric result implies a degree of crystallinity of about 75% for the native polymer. The degree of crystallinity of the latter is known to exceed 60% since that value was obtained upon recrystallizing a molded sample.

The agreement found between calculated and observed melting point depressions shows that the irregularities present in neoprene rubbers are randomly distributed. Further, this agreement indicates an internal self-consistency in the T_m and analytical data which supports, and indeed requires, the unexpectedly high value of T_m^0 found for the stereoregular polymer.

Glass Transition Temperatures

The glass temperatures of polychloroprenes varying in composition from

100% cis- to 100% trans-1,4 content are presented in Fig. 9. Measurements were made with the forerunner [7] of the Du Pont TMA module and were confirmed in most cases by DTA. The value shown for cis-1,4-poly(chloroprene) was subject to a larger error than that appropriate to the other

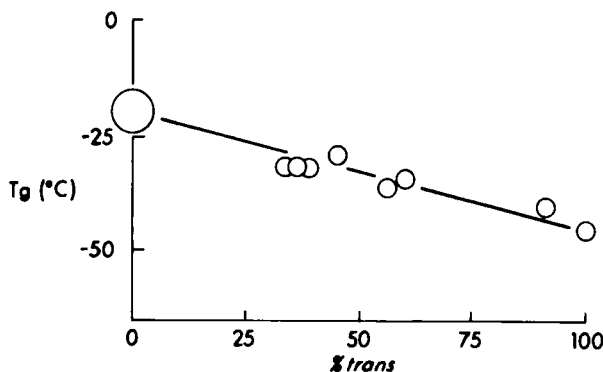


Fig. 9. Glass transition temperatures of polychloroprenes of varying trans content.

materials, and this is indicated by use of a larger circle in Fig. 9. The value plotted for this material is the mean of several values found for samples differing slightly in preparation. The larger error is attributable to minor discrepancies in structure and molecular weight. The data of Fig. 9 generally refer to polychloroprenes having molecular weights in excess of about 10,000. Scattered values available in the literature [33, 34] are in substantial agreement with the data of Fig. 9.

The data show no anomaly: the line in Fig. 9 is that calculated from the equation of Gordon and Taylor [35]

$$T_g = \frac{T_{g1} + (K T_{g2} - T_{g1})V_2}{1 + (K - 1)V_2}$$

with the assumption that the expansion coefficients of the cis- and trans-isomers are equal ($K = 1$). T_{g1} and T_{g2} are the glass temperatures of the trans- and the cis-isomers, and V_2 the mole fraction of cis-isomer present.

Electron Micrographs of Crystals of Stereoregular Polymer

A single crystal of stereoregular polymer prepared as set forth in the Experimental Section is shown in Fig. 10 at a magnification of 50,000X.

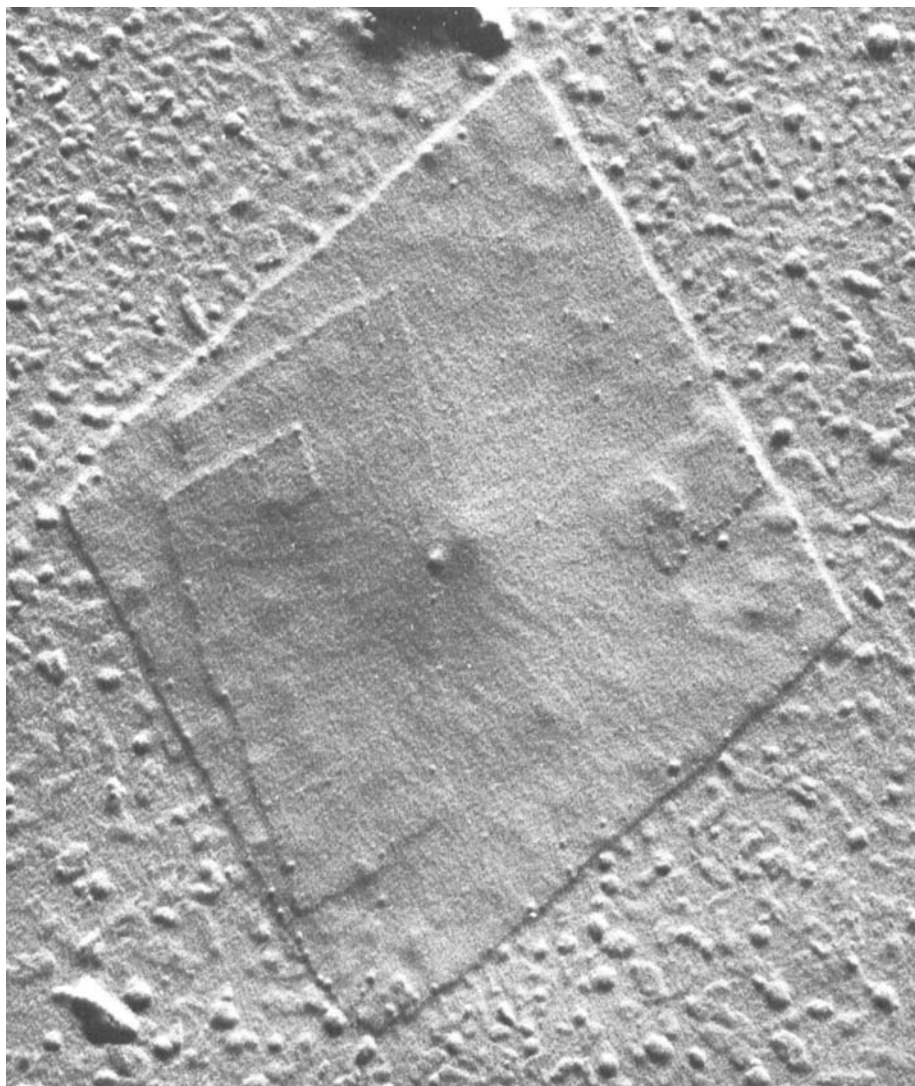
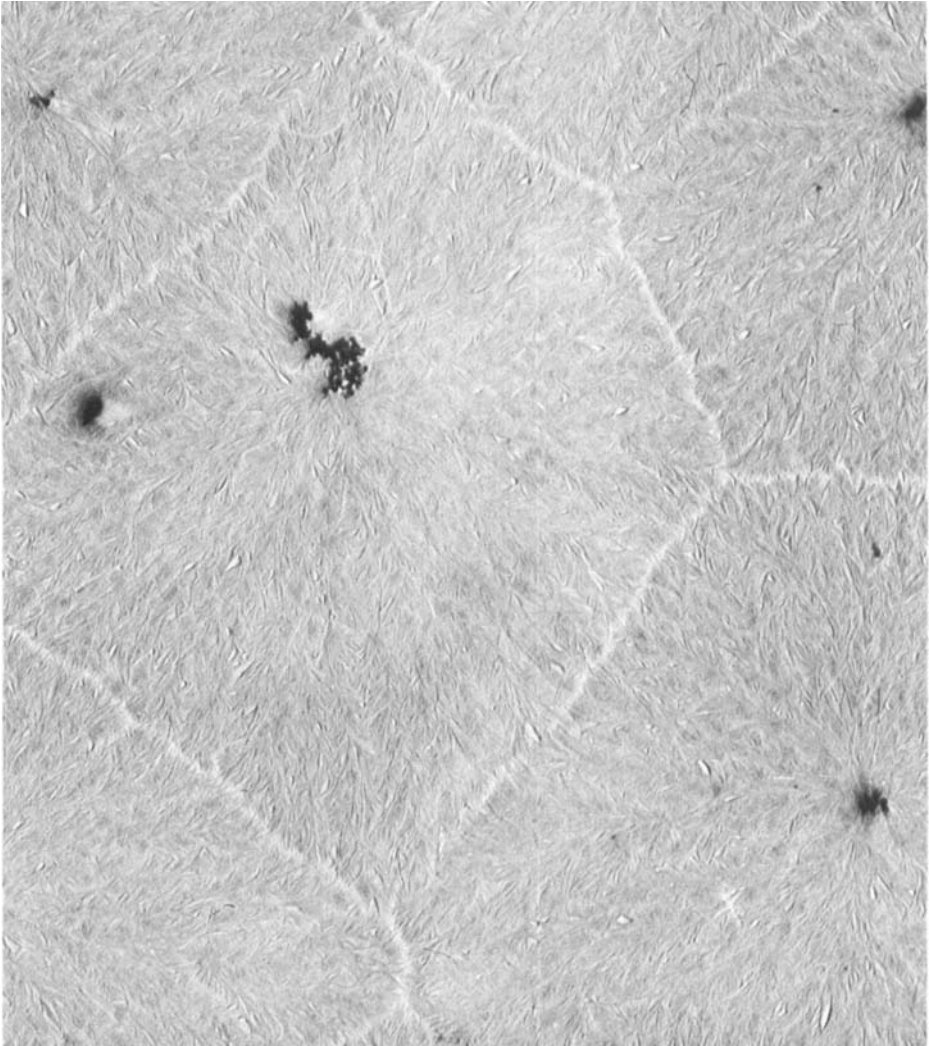


Fig. 10. Electron micrograph of single crystal of stereoregular polymer
50,000X.

It is approximately 200 Å thick. Electron diffraction experiments were not carried out with this preparation. Many spirals, closed loops, and overgrowths were found, along with radial striations presumably attributable to slight puckering when the crystal was deposited on a flat substrate.



1 μ

Fig. 11. Electron micrograph of spherulites of stereoregular polymer quenched at 0°C.

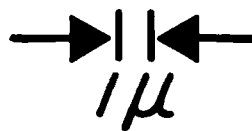
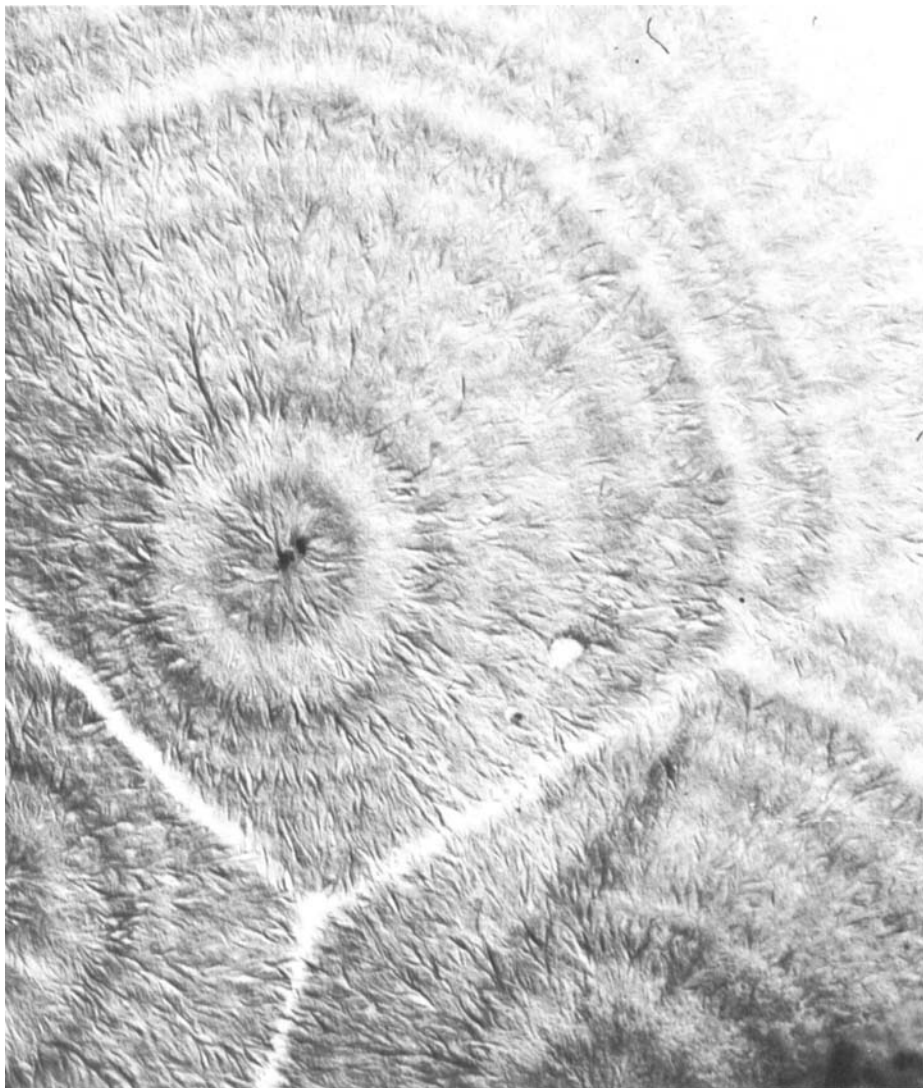


Fig. 12. Electron micrograph of spherulites of stereoregular polymer formed by annealing at 25°C.

Spherulites prepared from more concentrated solution as described in the Experimental Section are shown in Figs. 11 and 12. Those in Fig. 11 resulted from shock cooling in ice water followed by slow evaporation of solvent. Spherulites shown in Fig. 12 were similarly formed after slow cooling to room temperature. The latter figure shows the concentric banding which results from slower crystallization at the higher temperature.

ACKNOWLEDGMENTS

Our thanks are extended to Drs. R. C. Ferguson, D. B. Pattison, C. W. Stewart, H. A. Davis, and R. D. Souffie for their contributions to this work.

REFERENCES

- [1] J. T. Maynard and W. E. Mochel, *J. Polym. Sci.*, **13**, 235 (1954).
- [2] P. J. Flory, *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca, New York, 1953, pp. 573 and 244.
- [3] A. N. Gent, *J. Polym. Sci., Part A*, **3**, 3787 (1965).
- [4] F. Gornick and L. Mandelkern, *J. Appl. Phys.*, **33**, 907 (1962).
- [5] D. B. Pattison, Elastomer Chemicals Dept., E. I. du Pont de Nemours and Co., Private Communication.
- [6] P. W. Bridgman, *Proc. Amer. Acad. Arts Sci.*, **60**, 303 (1925).
- [7] R. R. Garrett, *Rubber Plastics Age*, **46**, 915 (1965).
- [8] R. C. Ferguson, *Kaut. Gummi, Kunstst.*, **11**, 723 (1965).
- [9] R. C. Ferguson, *Trans. N. Y. Acad. Sci., Series II*, **29**, 495 (1967).
- [10] R. C. Ferguson and W. D. Phillips, *Science*, **157**, 257 (1967).
- [11] R. C. Ferguson, *J. Polym. Sci., Part A*, **2**, 4735 (1964).
- [12] R. C. Ferguson, *Anal. Chem.*, **36**, 2204 (1964).
- [13] L. Mandelkern, R. R. Garrett, and P. J. Flory, *J. Amer. Chem. Soc.*, **74**, 3949 (1952).
- [14] P. J. Flory, R. R. Garrett, S. Newman, and L. Mandelkern, *J. Polym. Sci.*, **12**, 97 (1954).
- [15] M. L. Dannis, *J. Appl. Polym. Sci.*, **1**, 121 (1959).
- [16] Y. Sakai, *J. Polym. Sci., Part A-1*, **7**, 3198 (1969).
- [17] G. M. Schmidt et al., *J. Chem. Soc.*, **1964** (1966).
- [18] H. Morawetz, *Polymer Preprints*, **5**, 975 (1964).
- [19] G. Adler, *J. Chem. Phys.*, **31**, 848 (1959).
- [20] G. Adler, D. S. Ballantine, and B. Baysal, *J. Polym. Sci.*, **48**, 195 (1960).

- [21] G. C. Eastmond, *J. Appl. Chem.*, **13**, 221 (1963).
- [22] K. Hayashi and S. Okamura, *Makromol. Chem.*, **47**, 231 (1961).
- [23] C. W. Bunn, *Proc. Roy. Soc., Ser. A.*, **180**, 40 (1942).
- [24] J. I. Lauritzen and J. D. Hoffman, *J. Res. Nat. Bur. Stand., A*, **64**, 73 (1959).
- [25] L. Mandelkern, *J. Polym. Sci.*, **47**, 494 (1960).
- [26] G. M. Gopalan and L. Mandelkern, *J. Phys. Chem.*, **71**, 3833 (1967).
- [27] E. G. Lovering and D. C. Wooden, *J. Polym. Sci., Part A-2*, **7**, 1033 (1969).
- [28] J. P. Bell and J. H. Dumbleton, *J. Polym. Sci., Part A-2*, **7**, 1033 (1969).
- [29] J. T. Maynard and W. E. Mochel, *J. Polym. Sci.*, **13**, 251 (1954).
- [30] R. C. Ferguson, Central Research Dept., E. I. du Pont de Nemours and Co., Private Communication.
- [31] P. J. Flory, *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca, New York, 1953, p. 569.
- [32] R. D. Souffie, Elastomer Chemicals Dept., E. I. du Pont de Nemours and Co., Private Communication.
- [33] R. Nagao, *Polymer*, **9**, 517 (1968).
- [34] C. Aufdermarsh and R. Pariser, *J. Polym. Sci.*, **A2**, 4727 (1964).
- [35] M. Gordon and J. S. Taylor, *J. Appl. Chem.*, **2**, 493 (1952).

Accepted by editor May 6, 1970

Received for publication June 3, 1970

NOTE ADDED IN PROOF

Subsequent to our submission of the foregoing article, other investigators have published T_m^* vs. T_c data for both a sample of our stereoregular polymer and for Neoprene HC [W. R. Krigbaum and J. H. O'Mara, *J. Polym. Sci., Part A-2*, **8**, 1011 (1970)]. Except for their 2 or 3 highest points for the stereoregular sample which do conform with our data shown in Fig. 4—points at which crystallization is very slow—their data all lie at a much lower slope than do ours, and they are therefore interpreted through the use of a relationship different from our Eq. (1). Krigbaum and O'Mara employed dilatometry to secure their data. We have listed our objections to the use of conventional dilatometry for this purpose on p. 1690 and believe that the discrepancies between the two sets of data are due to this cause.