

Suspension Bromination of High-Density Polyethylene

NESTOR A. ARROYO* and ANNE HILTNER, *Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106*

Synopsis

High-density polyethylene powder has been brominated in suspension. The product was characterized by various physicochemical methods to determine the nature and effect of the substitution. Analysis of the infrared spectra indicates an initial addition reaction to terminal vinyl double bonds, followed by a substitution reaction on the polymer chain. The kinetic and thermal data show that the pseudo-first-order reaction occurs in the amorphous regions only. The brominated sites function as chain defects to decrease the crystallinity of the melt-recrystallized polymer, prevent annealing, and cause intensity changes in the mechanical α relaxation. Limits are observed in these effects, however, which confirms the expected "blocky" rather than random nature of the substitution.

INTRODUCTION

Nondestructive methods for chemical modification of polyethylene have been used for property development. Halogenation is frequently employed for this purpose. As expected, modification generally results in a material with lower crystallinity, and elastomers derived from polyethylene have been prepared by chlorination and chlorosulfonation.¹⁻⁵ The selectivity of chemical attack on a crystalline polymer for the amorphous regions gives an added versatility to the nondestructive halogenation reaction. The physical and mechanical properties of suspension-chlorinated spherulitic polyethylene have been reported to differ significantly from those of randomly substituted polyethylene with the same amount of chlorine.⁶ It was postulated that the amorphous regions were preferentially attacked to produce a material with "blocky" substitution.

The various morphological forms of polyethylene can be used to obtain "copolymers" by chemical modification which vary greatly in distributional characteristics. Halogenation of single crystals produces essentially a regular copolymer with one comonomer about every 60th repeat unit.⁷ Regular substitution somewhat similar to that obtained with single crystals is thought to be produced by halogenation of nascent polyethylene "shish kabobs."⁸ Halogenation in solution produces a material with a more random distribution of substituted sites.⁹

In this paper we report the physical and mechanical characterization of modified spherulitic polyethylene. The bromination reaction has been utilized to introduce a relatively large substituent at the reaction site in order to emphasize the distributional effects.

* Present address: David Sarnoff Research Institute, RCA Corporation, Princeton, New Jersey 08540.

EXPERIMENTAL

The material used for bromination was Marlex 6015, a high-density linear polyethylene ($M_w = 10^6$). The polymer was ground at low temperatures. Pellets of the polymer were cooled to liquid nitrogen temperatures before being fed between the grinding wheels; however, it is estimated that the polymer is actually at about 0°C during the grinding process. Figure 1 shows an optical micrograph of the particles under cross polaroids. The particles have a size distribution that varies between 70 and 700 microns, peaked around 250 microns. The ground polymer was washed several times with a 1:1 mixture of water-acetone to eliminate contamination from the grinding process. It was then dried at vacuum for 25 hr at 60°C.

The ultraviolet-catalyzed bromination was carried out in different suspending agents and under various temperature conditions. Suspending agents such as carbon tetrachloride and tetrachlorethane led to polymer contamination. Chlorine which could not be removed from the product by washing was detected by elemental analysis and infrared spectroscopy, and was attributed to ultraviolet-catalyzed side reactions with the suspending agent. Bromobenzene was found to be a suspending agent that did not produce any detectable side reactions.

In a typical reaction, 10g of the dried polymer was placed in a three-neck reaction flask with 500 ml certified reagent-grade bromobenzene and 50 ml elemental bromine. The flask had adaptors for the placement of an ultraviolet lamp, for a nitrogen inlet, and for sample extraction.



0.5 mm

Fig. 1. Optical micrograph of the cryogenically ground polyethylene particles taken with crossed polarizers.

A constant nitrogen flow was used to eliminate moisture and oxygen from the reaction and prevent chain scission via the formation of peroxides and hydroperoxides. Any degradation was detected by the presence of carbonyl absorbances in the infrared spectrum. The suspension was magnetically stirred and placed in a constant-temperature bath at 50°C. Samples were taken at different times after the ultraviolet lamp was switched on. The product was separated from the suspending medium in a separatory funnel and washed several times with fresh bromobenzene until the solvent appeared free of bromine. It was then washed with acetone and ether to remove bromobenzene. Finally, it was vacuum dried at 40°C for 48 hr.

The bromine content was established by x-ray fluorescence. A General Electric x-ray spectrometer was used. The machine was calibrated for bromine content and thickness of the sample. The polymer was compression molded into discs 1 cm in diameter and 0.3–0.5 mm thick. Specimens were molded at 150°C and 45 kbar pressure for 1 min. The mold was removed from the press and quenched in ice water. Compression molding for times longer than 1 min produced degradation and dehydrobromination of the samples. This was the standard procedure used in the preparation of all compression-molded specimens.

Films 0.04 ± 0.005 mm thick for infrared analysis were prepared as described above. The infrared absorption spectra were measured in a Digilab F.T.S. 14. The spectra were recorded in the wavenumber region between 400 and 3800. Fifty scans in this region were allowed for both sample and reference. For quantitative comparison of band intensities the band at 1303 cm^{-1} was taken as a reference absorption. This band is due to twisting of methylene units,¹⁰ and its intensity does not change with hydrogen substitution of some of these units.

The heats of melting and melting points were recorded on a Perkin-Elmer DSC 2 instrument. Sample weights ranged from 4 to 7 mg weighed with a 1% accuracy. In order to express the heats of melting in calories per grams of equivalent $-\text{CH}_2-$ units, the bromine content was subtracted from the sample weight and replaced by the equivalent weight of hydrogen. The heating rate was 20°C/min; the instrument was calibrated from the melting temperature and the heat of fusion of a known weight of indium. The reported heats of melting are average values of at least two runs. The standard deviation is ± 2 cal/g. The melting points were established by superimposing, on the polymer thermograms, the leading edge of an indium fusion peak scanned under the same heating conditions as the polymers. The intercept of the leading edge with the baseline was taken as the melting temperature. The reported melting temperatures are averages of at least two runs. The standard deviation for each average is $\pm 0.5^\circ\text{C}$.

Melting points and heats of melting were determined for the brominated powders "as prepared." Once the melting had occurred, the samples were heated to 150°C and then cooled from the melt to room temperature at 20°C/min. These samples are reported as "melt recrystallized." Their heats of melting and melting points were measured under the same conditions reported for the "as prepared" samples.

The dynamic mechanical properties were studied with an inverted torsional pendulum which operates at a frequency of about 1 Hz over the temperature range of -185° – 115°C . The samples were films 5 cm long, 0.4 cm wide, and 0.25

± 0.05 mm thick. The films were compression molded in the way previously described and annealed for 3 hr at 120°C under vacuum. The heats of melting of these films were determined under the same conditions as those reported for the "as prepared" and "melt recrystallized" samples.

RESULTS AND DISCUSSION

Kinetics

The percentage by weight of bromine in the ground polyethylene versus the reaction time at 50°C is shown in Figure 2. The fact that the last two points are separated by 100 hr while the bromine uptake increases only by 1% indicates that a saturation of the available sites for bromination is being reached. The rate of bromination is temperature dependent. Another reaction carried out under the same conditions at 25°C showed an uptake of 2% bromine after 150 hr of reaction. Previous workers^{7,9} have shown that in suspension bromination of polyethylene single crystals, there is rapid initial reaction as the crystal folds are saturated by bromine. The time required for saturation at room temperature was found to be around 50 hr.

Due to the fact that both bromine and polyethylene were present in excess, the reaction was analyzed in terms of the concentration of products. For the reaction $A \rightarrow B$, where A is the reactant and B the product, the first-order rate expression in terms of the product concentrations is

$$\frac{dx}{dt} = k(a - x) \quad (1)$$

where x is the ratio of $-\text{CHBr}-$ to unreacted $-\text{CH}_2-$ at time t and a is the ratio of $-\text{CHBr}-$ to $-\text{CH}_2-$ at saturation. Upon rearranging and integrating, eq. (1) becomes

$$kt = \ln[a/(a - x)] \quad (2)$$

Table I shows the number of $-\text{CH}_2-$ units per $-\text{CHBr}-$ that corresponds to the different bromine uptakes. Each $-\text{CHBr}-$ can be considered a brominated site. The inverse of these values is the number of $-\text{CHBr}-$ per $-\text{CH}_2-$ units or the concentration of reacted sites in the polymer chain, x . The extrapolation of x to infinite time gives the saturation concentration of the product,

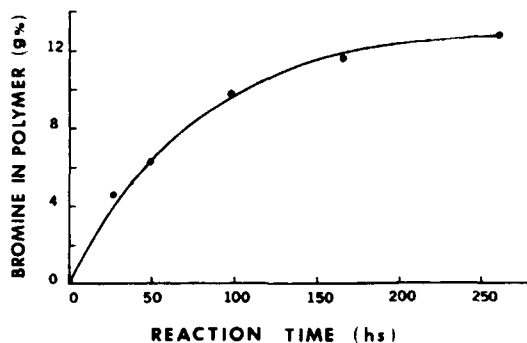


Fig. 2. Rate of bromine uptake.

TABLE I
Composition of Brominated Polyethylene Samples

Time, hr	Bromine, wt-%	No. of —CH ₂ — units per —CHBr—	x	$a - x$
0	0.0	∞	0.0000	0.0270
27	4.7	115	0.0087	0.0183
49	6.3	85	0.0118	0.0152
98	9.7	53	0.0189	0.0081
166	11.5	45	0.0227	0.0043
261	12.7	39	0.0256	0.0014
500	extrap.	37	0.0270	0.0000

a. Five-hundred hours was considered sufficient to reach the saturation point.

Table I also shows the numerical values of the various parameters in the first-order kinetic equation. The plot of $\ln[a/(a - x)]$ versus time (Fig. 3) fits a linear regression with a standard deviation of 0.05 and a correlation coefficient of 0.999. The value of the rate constant obtained from the slope is $(11.2 \pm 0.3) \times 10^{-3} \text{ hr}^{-1}$. It was concluded that, within experimental error, the production of brominated methylene units, —CHBr—, follows pseudo-first-order kinetics.

Infrared Analysis

The infrared spectra of the brominated and unbrominated polyethylenes in the region between 400 and 2000 cm^{-1} are shown in Figure 4. Three main features are of interest. The first concerns the possibility of side reactions with solvent and polymer degradation. Bromobenzene has strong aromatic absorption in the region between 1000 and 1100 cm^{-1} which is not present in the modified polymers. Degradation and oxidation would appear in the form of strong carbonyl absorptions¹⁰ in the wavenumber region between 1680 and 1730. These bands are not present after 261 hr of reaction. Thus, it was concluded that the reaction is clean with regard to solvent contamination and oxidative degradation.

The second aspect to be considered is the bromination of the terminal vinyl double bonds. Bands due to terminal vinyl double bonds are present at 909, 990,

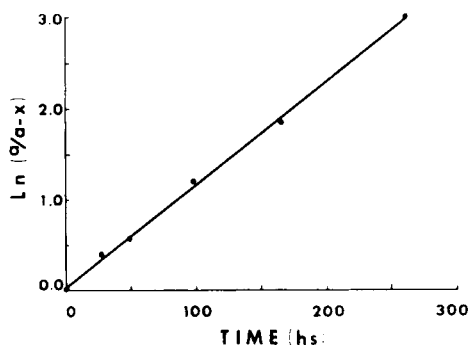


Fig. 3. Plot of the kinetic data from eq. (2).

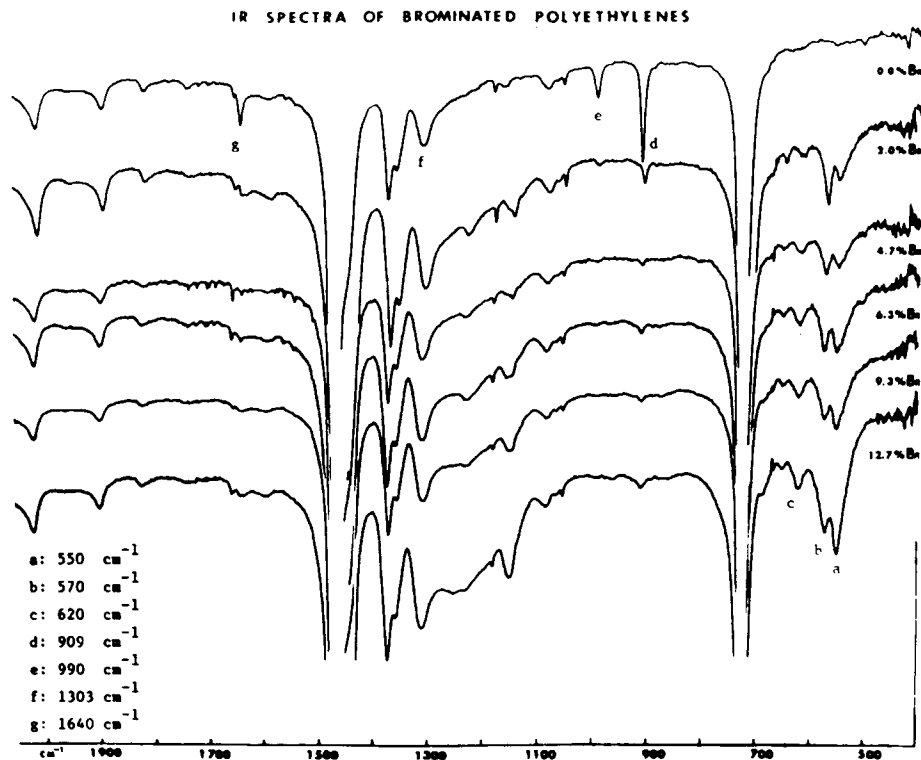


Fig. 4. Infrared spectra of the brominated polyethylene:

and 1640 cm^{-1} ; the one at 909 cm^{-1} is the strongest.¹⁰ These bands are almost gone after 2% bromine uptake. However, a weak band at 909 cm^{-1} is still detected when the bromine uptake is 12.7%. Although a quantitative study of the double bond absorbance intensity was not made, qualitatively these results agree with those of Keller et al.¹¹ In treating polyethylene single crystals with ozone, they found that 90% of the chain ends reacted very rapidly and were assumed to be excluded from the single crystals.

Three bands are observed in the C-Br stretching region at 550, 570, and 620 cm^{-1} . Band assignments were based on the literature for low molecular weight brominated aliphatics.¹²⁻¹⁴ Compounds of the type $\text{CH}_3-(\text{CH}_2)_n-\text{CH}_2\text{Br}$ have a band in the region of $570 \pm 5\text{ cm}^{-1}$, and compounds of the type $\text{CH}_3-(\text{CH}_2)_n-\text{CHBr}-\text{CH}_3$ have a band in the region of $550 \pm 5\text{ cm}^{-1}$. Therefore, the band at 570 cm^{-1} was assigned to C-Br stretching of terminal carbons, while the band at 550 cm^{-1} was assigned to C-Br stretching of secondary carbons. The band at 620 cm^{-1} could not be assigned by comparison with low molecular weight brominated aliphatics.

Figure 5 shows the relative absorbance of the 550 and 570 cm^{-1} bands versus the bromine uptake. The relative absorbance of the band at 570 cm^{-1} does not change above 2% bromine. Since the unsaturation also disappears early in the reaction, there is little doubt that the initial bromination reaction is addition to terminal vinyl groups to give vicinal $-\text{CHBr}-\text{CH}_2\text{Br}$. The relative adsorbance of the 550 cm^{-1} unit band represents the extent of the slower substitution reaction in which $-\text{CHBr}-$ groups are formed. Within experimental error,

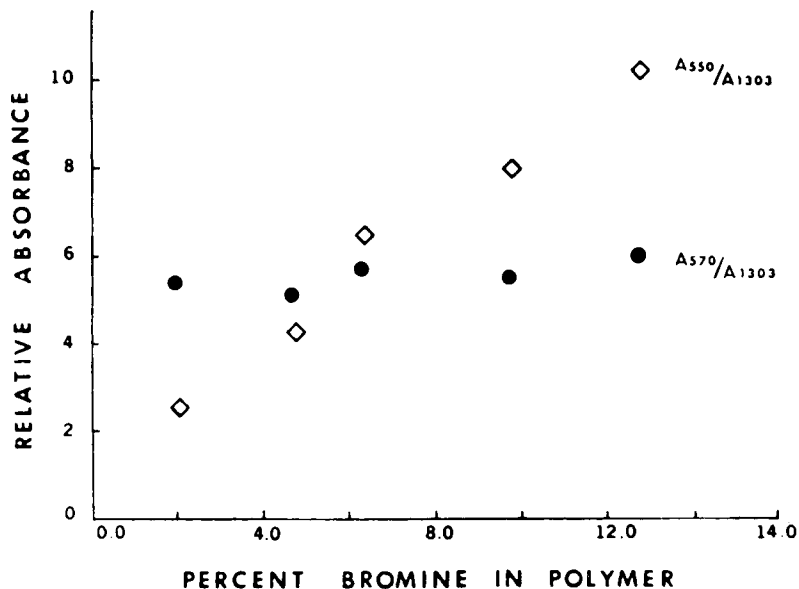


Fig. 5. Relative intensities of the primary (570 cm^{-1}) and secondary (550 cm^{-1}) carbon-bromine frequencies.

the relative absorbance of the band at 550 cm^{-1} increases linearly with bromine content above 2%.

In summary, infrared study shows that the bromination occurs initially by addition to the vinyl double bonds followed by substitution on the polymer chain. The former reaction involves a total bromine uptake of less than 2%. The fact that most of the terminal double bonds are brominated indicates that bromination takes place inside the particles as well as on the surface.

Thermal Analysis

In order to determine the effect of bromination upon the crystallinity of the starting material, the heats of melting and the melting points of the brominated polymers were measured. Figure 6 shows the plot of the heat of melting versus the bromine uptake for the materials "as prepared" and "melting recrystallized." The plot shows that the heat of melting of the material "as prepared" does not

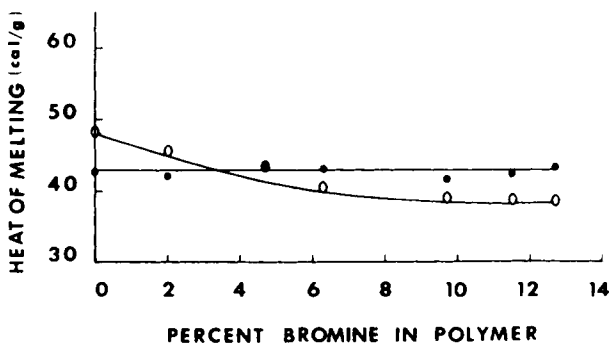


Fig. 6. Heat of melting of brominated polyethylene: (●) as prepared; (○) melt recrystallized.

change upon bromination. It is concluded that bromination takes place only in the amorphous regions of the particles. This is analogous to the single crystals where it was shown that the bromination takes place on the fold surfaces.^{7,9}

The behavior of the "melt-recrystallized" specimens is different. The "melt-recrystallized" heat of melting for the unbrominated polymer is higher than the "as prepared" one. This difference decreases steadily with increasing bromine content, and above 4% bromine the "melt-recrystallized" specimen has a lower heat of melting than the "as prepared" specimen. Above 6% bromine the values remain practically constant at 39 cal/g.

The unbrominated polymer shows an increase in the heat of melting probably because the recrystallization is carried out at a cooling rate that produces a higher supercooling temperature than that of the original polymer. The result is a material with a higher degree of crystallinity. The increase in the crystallinity is achieved at the expense of the previously amorphous regions of the starting material. However, when bromine is incorporated into the amorphous regions this material may no longer be able to crystallize. The bromine atom has a van der Waals radius of 1.95 Å, thus it cannot cocrystallize with the methylene units without producing a large defect in the crystal. The depression of the heat of melting in the "melt-recrystallized" materials is consistent with the exclusion of bromine atoms from the crystals. The decrease in crystallinity is approximately linear with bromine up to 6% bromine content. Above this, the crystallinity of the melt-recrystallized materials remains almost constant. If the decrease in the heat of melting is determined by the number of defects, it seems that above 6% bromine uptake the number of defects remains constant. Since only the amorphous regions are available for reaction, additional substitution may occur close to a carbon atom which already contains a bromine atom, and a blocky rather than random structure is produced.

Table I shows the number of $-\text{CH}_2-$ units that would be between each substituted carbon if the substitution were uniformly distributed along the polymer chain. Taking into account the lamellar thickness of bulk-crystallized polyethylene, between 140 Å (from electron microscopy) and 210 Å (from small-angle x ray),¹⁵ and considering that the length of a methylene unit is¹⁶ 1.27 Å, the number of methylene units in the lamellae will be between 110 and 165. Since the crystalline regions are not reacted, it can be seen that after the bromine uptake is around 5%, subsequent bromination has to take place close to a site that is already substituted. In this way the proposition that size of the defect regions increases while the number remains constant is consistent with the observation that only the amorphous regions are brominated.

The effect of thermal history was demonstrated by recrystallizing at different cooling rates. The cooling rates ranged from 0.31° to 320°C/min. The lower cooling rate produces an effect similar to isothermal crystallization, while the faster cooling rate resembles fast quenching. The materials examined had bromine contents of 0.0%, 6.3%, and 12.7%. The heats of melting were determined using a heating rate of 20°C/min, as in the previous experiments.

Figure 7 shows the plot of the heat of melting for these three materials versus the logarithm of the cooling rate. It can be seen that an annealing effect is present for the unbrominated samples. There is a gradual increase of the heat of melting as the cooling rate is decreased. The annealing effect is considerably less for the sample with 6.3% bromine, and no annealing can be detected for the

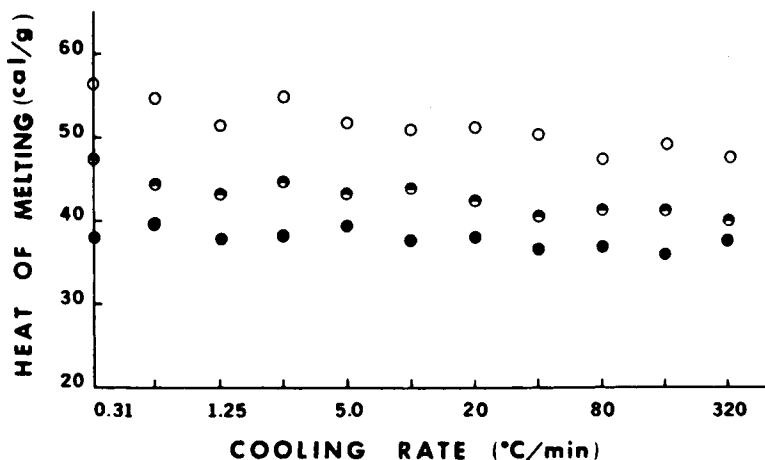


Fig. 7. Cooling rate dependence of the heat of melting: (O) 0.0% Br; (◐) 6.3% Br; (●) 12.7% Br.

sample with 12.7% bromine. It is postulated that the annealing process is prevented by the bromine substitution in the same way that it is by selective oxidation¹⁷ or by crosslinking the amorphous regions with high-energy radiation.^{17,18} In each case the reacted group cannot be incorporated into the crystal, and lamellar thickening is inhibited since the chains are no longer free to be pulled through the crystal.

The melting points of the modified polymers were also determined, and Figure 8 shows the plot of the melting temperature of brominated polyethylene versus the bromine content for the materials "as prepared" and "melt recrystallized." In both cases the melting point decreases up to 6% bromine and then remains constant.

In general, noncrystallizable comonomeric units have the effect of lowering the melting point. Flory has shown that under equilibrium conditions the melting point depression is given by¹⁹

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{R}{H_f} \ln p$$

where T_m and T_m^0 are the melting points of copolymer and homopolymer respectively, H_f is the heat of fusion per mole of crystallizing unit, and p is the

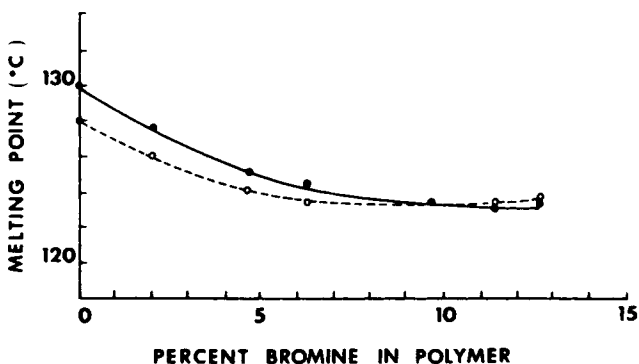


Fig. 8. Melting temperature of brominated polyethylene: (- -O - -) as prepared; (- ● -) melt recrystallized.

sequence propagation probability. The melting temperature depends on the sequence parameter p but not otherwise on the nature of the comonomer. For random copolymers, p can be identified with X_A , the mole fraction of crystallizable units. For an ordered or blocky copolymer, p will greatly exceed X_A , and the melting point depression will be less than that for random copolymers.

Because the melting temperatures were not obtained under equilibrium conditions, the data are not quantitatively compared with the theory. However, the observed behavior is consistent with formation of a blocky structure as described above. It is proposed that initially bromine substitution occurs essentially at random and the melting point correspondingly decreases. At about 6% a transition occurs where bromination can only take place close to a site already brominated. The number of noncrystallizable units no longer increases and the melting point remains constant.

Dynamic Mechanical Properties

The dynamic mechanical properties were studied in samples prepared as described in the experimental section. The heats of melting of these samples show no significant differences with those measured for the melt-recrystallized samples, except for the unbrominated material where there was an increase of 5 cal/g in the heat of melting. This behavior was expected; the crystallinity changes upon different cooling rates have already shown that annealing only takes place in the unbrominated materials. The spherulitic structure of the films was observed by optical microscopy under crossed polaroids. Figure 9 shows the changes in the spherulitic size upon bromination. There is a decrease in the spherulitic size with increase in the bromine content although there is no significant change in the heat of melting when the bromine uptake goes from 6.3% to 12.7%.

High-density polyethylene shows two main relaxation regions, α and γ . The

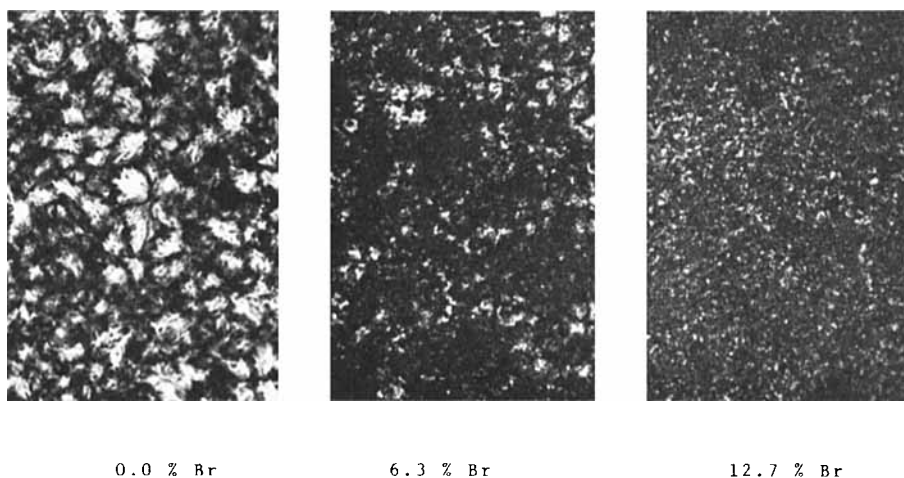


Fig. 9. Spherulitic morphology of films prepared from brominated polyethylene. The optical micrographs were taken with crossed polarizers.

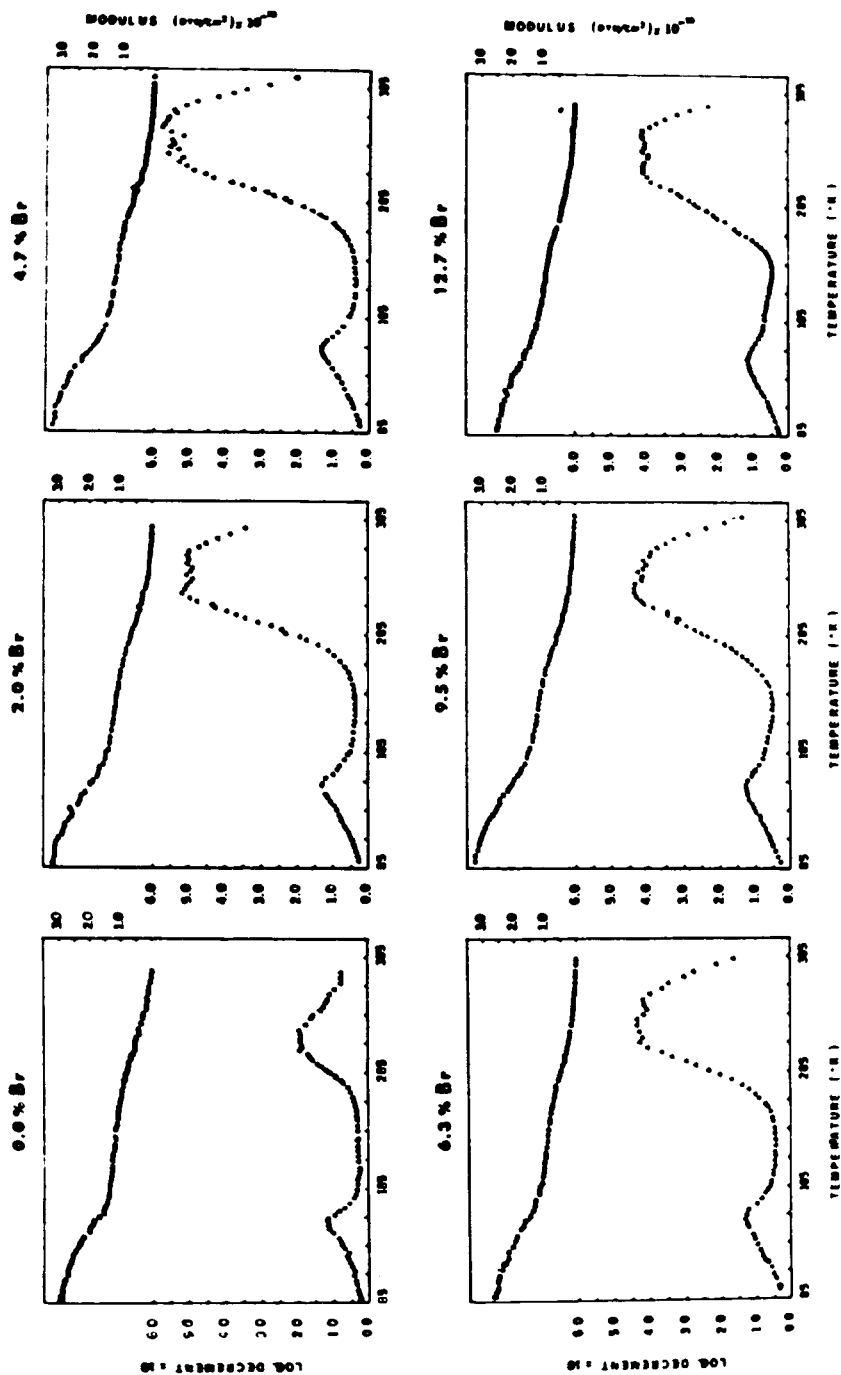


Fig. 10. Dynamic mechanical loss spectra of brominated polyethylene.

relaxation spectra of the brominated polyethylenes are shown in Figure 10. The recorded values are the logarithmic decrement and the elastic modulus versus the temperature. The γ relaxation appears around 150°K. The temperature and the intensity remain essentially constant with the increase in bromine content, but some broadening of the relaxation peak can be observed.

The most significant changes in the relaxation spectra upon bromination appear in the region of the α transition. Two peaks are distinguished in this region and are designated α_c and α_a , α_c being the one at higher temperature. A possible third peak is seen in the samples with high bromine content. The presence of fine structure in the polyethylene α relaxation at 1 Hz has also been reported by Illers²⁰ and Iwayanagi.²¹ The peaks were resolved by curve fitting. Table II shows the maximum intensity and the temperature (T_{\max}) for both peaks. T_{\max} for α_c remains constant at around 350°K. In the unbrominated material, T_{\max} for α_a is 316°K, increases to 327°K for the material with 4.7% bromine, and remains essentially constant at higher bromine content. The intensity of both α_c and α_a peaks shows a sharp increase when the bromine uptake goes from 0% to 2%. The intensity reaches a maximum when the bromine uptake is 4.7%, then decreases slightly and remains practically constant with subsequent increases in the bromine content. The increase in the α relaxation intensity occurs over the same range of bromine content as the decrease in the heat of melting.

Iwayanagi et al.²¹ have proposed that the primary α process in melt-recrystallized polyethylene (α_a) is due to slip in the amorphous regions as the lamellae slide past one another to assume reoriented positions. Stein²² has supported this interpretation by following the time-dependent changes in the average crystal lattice orientation as the polymer was heated through the α relaxation. Our results, which show an increase in α_a intensity with increasing amorphous content, are consistent with Iwayanagi's theory. The accompanying shift in α_a temperature from 316° to 325°K suggests that motion of the amorphous chain segments is hindered by bromine substitution.

It is generally agreed that the α_c represents a crystalline process. The temperature of the α_c does not shift with bromination which supports our hypothesis that bromine is excluded from the crystal lattice. Several theories of the α_c have been proposed. The increase in α_c intensity can be accounted for either in terms of axial rotation coupled to the amorphous regions²³ or lattice defect mechanisms where the defects ordinarily would be removed by annealing but remain in the brominated polymer because the annealing processes are inhibited.²⁰

TABLE II
Temperature and Maximum Intensity of the α Transition Peaks

Bromine, %	α_c		α_a	
	T_{\max} , °K	Log. dec.	T_{\max} , °K	Log. dec.
0	349	0.11	316	0.19
2	347	0.50	321	0.52
4.7	450	0.58	327	0.56
6.3	348	0.41	326	0.43
9.5	350	0.41	325	0.44
11.3	350	0.39	325	0.42
12.7	349	0.40	323	0.41

CONCLUSIONS

The suspension bromination of spherulitic polyethylene powders has been described. The reaction conditions employed result in a product that is free of degradative oxidation and chemical contamination.

Bromination was found to occur only in the amorphous regions of the polymer. The terminal vinyl double bonds are brominated early in the reaction and account for a bromine uptake of less than 2%. Further reaction occurs by substitution. The reaction follows pseudo-first-order kinetics in the production of brominated methylene units, —CHBr—.

The reaction conditions produce a polymer with "blocky" rather than random substitution. The blocks constitute chain defects which reduce the crystallinity of the polymer, prevent annealing, and cause intensity changes in the mechanical α relaxation. The magnitude of these effects is limited by the number of blocks since even the most highly brominated materials contain unmodified chain segments which are long enough to crystallize. When compared to conventional solution procedures for halogenated polyethylene, which produce essentially randomly substituted materials, the suspension method can be a means to highly modified materials with enhanced crystallinity-dependent properties.

The authors wish to thank Professor P. J. Phillips for his helpful comments.

References

1. K. Schmieder and K. Wolf, *Kolloid-Z.*, **134**, 149 (1953).
2. S. Matsuoka, R. J. Roe, and H. F. Cole, in *Diel. Prop. Polym. Symp.*, F. E. Karasz, Ed., Plenum Press, New York, 1971.
3. Kalfoglou and H. L. Williams, *Polym. Eng. Sci.*, **12**, 3 (1972).
4. G. Humbert, B. M. Quenum, P. Berticat, and G. Vallet, *Makromol. Chem.*, **175**, 1611 (1974).
5. C. R. Ashcraft and R. H. Boyd, *J. Polym. Sci., Polym. Phys. Ed.*, **14**, 2153 (1976).
6. P. J. Canterino and G. R. Kohle, *J. Appl. Polym. Sci.*, **6**, 20 (1962).
7. I. Harrison and E. Baer, *J. Polym. Sci. A-2*, **9**, 1305 (1971).
8. I. Harrison and E. Baer, *Polym. Lett.*, **9**, 843 (1971).
9. M. Equiluz and A. Hiltner, *Abstracts of 26th International Congress of Pure and Applied Chemistry*, Tokyo, 1977, p. 1273.
10. S. Krimm, *Adv. Polym. Sci.*, **2**, 51 (1960).
11. A. Keller and D. J. Priest, *J. Macromol. Sci. Phys.*, **B2**, 479 (1968).
12. J. K. Brown and N. Sheppard, *Proc. R. Soc. London, Ser. A*, **231**, 555 (1955).
13. J. K. Brown and N. Sheppard, *Trans. Faraday Soc.*, **50**, 1164 (1954).
14. F. E. Mortimer et al., *J. Am. Chem. Soc.*, **69**, 822 (1947).
15. R. G. Brown and R. K. Eby, *J. Appl. Phys.*, **35**, 4 (1964).
16. P. H. Geil, *Polymer Single Crystals*, Interscience, New York, 1963, p. 21.
17. K. H. Illers and H. Hendus, *Makromol. Chem.*, **113**, 1 (1968).
18. H. E. Bair, R. Salovery, and T. W. Huseby, *Polymer*, **8**, 9 (1967).
19. P. J. Flory, *J. Chem. Phys.*, **17**, 223 (1949).
20. K. H. Illers, *Rheol. Acta*, **3**, 202 (1964).
21. S. Iwayanagi and N. Nakana, *Rept. Progr. Polym. Phys. Japan*, **7**, 179 (1964).
22. R. S. Stein, *Polym. Eng. Sci.*, **8**, 259 (1968).
23. J. D. Hoffman, C. Williams, and E. Passaglia, *J. Polym. Sci. C*, **14**, 173 (1966).

Received February 14, 1978

Revised March 31, 1978