(27) F. E. Filisko, H. T. Kau, J. DeRudder, and J. Golba in "Structure-Solubility Relationships in Polymers", F. W. Harris and R. B. Seymour, Eds., Academic Press, New York, 1977, pp 59–70.
(28) F. Filisko and H. T. Kau, *J. Macromol. Sci., Phys.*, **14** (1), 173 (1977).
(29) C. E. Anagnostopoulos, A. U. Coran, and H. R. Gamrath, *J. Appl. Polym. Sci.*, **4**, 181 (1960).
(30) S. Krimm, J. J. Shipman, V. L. Folt, and A. R. Berens, *J. Polym. Sci., Part B*, **3**, 275 (1965).
(31) F. E. Filisko, research in progress.
(32) R. S. Raghava and F. E. Filisko, *J. Appl. Phys.*, **45** (10), 4155–4158 (1974).
(33) F. E. Filisko and H. T. Kau, *J. Macromol. Sci., Phys.*, **14** (1), 173–183 (1977).
(34) G. C. Alfonso, M. P. Verdona, and A. Wasiak, *Polymer*, 711–716 (1978).
(35) G. S. Y. Yeh and P. H. Geil, *J. Macromol. Sci., Phys.*, 1 (2), 251–277 (1967).

Solid Solution Formation and Fractionation in Quasi-Binary Systems of Polyethylene Fractions

Paul Smith† and R. St. John Manley*

Pulp and Paper Research Institute of Canada and Department of Chemistry, McGill University, Montreal, Canada. *Received November 10, 1978*

ABSTRACT: Solid solution formation and fractionation during crystallization were studied in two quasi-binary systems of polyethylene fractions by means of differential scanning calorimetry, X-ray scattering (wide and small angle), and microscopy. The molecular weights ($\bar{M}_n$) of these systems were: (1) 980 and 1790, and (2) 1790 and 20×10^3. At cooling rates lower than 20 °C/min fractionation occurred during the solidification process. The composite polymeric solids thus produced exhibited a eutectic-type melting point/composition diagram with the eutectic point located close to the axis of the constituent with the lowest molecular weight. These diagrams could be described with the well-known relation for the melting point depression according to Flory and Huggins, if the Flory–Huggins parameter had the value −0.02. Upon quenching to temperatures lower than 80 °C a continuous series of solid solutions were generated from the quasi-binary melts. The overall enthalpies of fusion of both the solid solutions and separate solid phases were found to depend linearly on the volume fraction of one of the components. The slowly cooled mixtures showed two SAXS-long periods that corresponded with the long periods in the pure fractions. The solid solutions were characterized by a new long spacing intermediate in length between the long periods of the fractions in the system (1) and exceeding those of the pure fractions in the system (2). The results are discussed in terms of structural differences between the solid solutions and the separate solid phases.

This paper deals with quasi-binary model systems that are composed of fractions of linear polyethylene with various molecular weights. It describes a study of the structure and properties of the solid solutions that are generated from the melt upon rapid cooling and of the composite solids produced at the low solidification rates where fractionation occurred during the crystallization process. The results are of interest in connection with the effect of the molecular weight distribution on the crystallization behavior and ultimate properties of polymeric materials.

Fractionation during crystallization of heterodisperse polymeric systems is a well-known phenomenon that originates in the mixing gap in the solid crystalline state of chain molecules differing sufficiently in length (see, e.g., ref 1–5). In a previous paper[6] it was shown that under thermodynamic equilibrium conditions a binary mixture of homologous chain molecules, such as, e.g., normal paraffins or polyethylene fractions with various molecular weights, solidifies to form two solid phases, if the requirement $\Gamma\Delta x > 2$ is satisfied. Here Δx denotes the difference in chain length of the constituent molecules, expressed as the number of segments. Γ is the lateral surface free energy per chain segment, divided by kT, where k is Boltzmann's constant and T is the absolute temperature. In binary systems with $\Gamma\Delta x \leq 2$ solid solutions are formed over the entire concentration range, and fractionation is not observed. Under nonequilibrium conditions, however, solid solutions may also form in systems of chain molecules that have a widely different length, i.e., $\Gamma\Delta x \gg 2$. This is bound to occur at relatively low solidification temperatures where the crystallization process proceeds so rapidly that the cross-diffusion of the molecules, which is an essential step in the fractionation, is impeded.

Since fractionation during crystallization of multicomponent polymeric systems was suggested in 1958 by Bunn et al.,[7] many studies have been devoted to this topic. It is observed in crystallization both from the melt[1,2,8] and from solution.[3,4,9] In a detailed study Mehta and Wunderlich[8] established quantitatively to what extent fractionation occurs during solidification of heterodisperse polyethylene samples at various crystallization temperatures. They arrived at the important conclusion that fractionation acts upon each molecule, and it is not impeded by the complex process of high-polymer crystallization under ambient conditions. Apart from studies by Kardos et al.[10] at elevated pressure and investigations on mixtures of low molecular weight *n*-paraffins,[11–14] most of the research on fractionation in heterodisperse systems has been carried out with polymer samples with rather broad molecular weight distributions. In these systems fractionation and solid-solution formation occur simultaneously, thus obscuring differences in the properties and structure of the solid solutions and the separate solid phases.

Accordingly, in the present study binary model systems were prepared from three fractions of linear polyethylene having number average molecular weights ($\bar{M}_n$) of 980, 1790, and 20×10^3. Since these fractions were not perfectly monodisperse in molecular weight the binary systems will be referred to as quasi-binary. It was shown earlier in a preliminary account of this work that at low cooling rates

† Central Laboratory, DSM, Geleen, The Netherlands.

0024-9297/79/2212-0483$01.00/0

Table I
Characteristics of Polyethylene Fractions

sample designation	M_n	M_w/M_n	T_m, °C	ΔH_u, kJ/mol
1000	980	1.1	105.0	3.37
2000	1790	1.1	120.5	3.60
20000	20×10^3	3.5	131.0	2.95

fractionation occurs during solidification of mixtures of these fractions.[15] However, upon rapid cooling, e.g., by quenching in cold water, the systems composed of the fractions 980/1790 and 1790/20×10^3 form a continuous series of mixed crystals. This paper deals with calorimetric, X-ray scattering, and density measurements and some morphological studies that were performed to elucidate some of the differences in the structure and properties of the separate solid phases and solid solutions composed of chain molecules differing substantially in length.

Experimental Section

Materials. The molecular characteristics of the polyethylene fractions used in this study are listed in Table I. As is customary $\bar{M}_n$ and $\bar{M}_w$ refer to the number and weight average molecular weight, respectively. The melting point (T_m) and the heat of fusion per structural unit (ΔH_u) of the original polymer samples are also given in Table I; these quantities were measured by differential scanning calorimetry (DSC). The low molecular weight fractions were purchased from Polysciences Inc. and were used as received. The fraction 20 000 was kindly supplied by the Dutch State Mines/DSM.

Specimens. Homogeneous solutions of the quasi-binary systems of polyethylene fractions were prepared by extensively mixing the powdered components. Subsequently the mixtures were heated for 1 h in sealed test tubes at a temperature that was 10 °C higher than the melting point of the higher melting constituent. The solutions thus prepared were cooled down to solidify at various rates that ranged from 0.2 °C/min to quenching in liquid nitrogen.

Differential Scanning Calorimetry. The crystallization and melting behavior of the polyethylene fraction systems were studied by differential scanning calorimetry. Samples of about 5 mg of the homogenized mixtures that were quenched in liquid nitrogen were sealed in aluminum pans and heated for 10 min at 150 °C. Subsequently the specimens were cooled down to solidify at various rates. Melting thermograms of the solidified mixtures were recorded at a speed of 10 °C/min, unless indicated otherwise. The transition temperatures quoted in this paper invariably refer to the peak temperatures in the thermograms. The calorimeter (Perkin Elmer DSC-Model 1B) was calibrated according to the standard procedures.

Scanning Electron Microscopy. The microstructures of the crystallized mixtures were studied in the scanning electron microscope (Cambridge Stereo-Scan Mark 11A) on fracture surfaces that had been obtained by breaking the specimens in liquid nitrogen.

X-ray Scattering. Small- and wide-angle X-ray scattering (SAXS and WAXS) experiments were performed at room temperature using Ni-filtered Cu Kα radiation, with the aid of a pinhole-collimated flat-film camera. A Seifert X-ray generator was operated at 40 kV and 20 mA. The specimens had a thickness of about 1 mm and the film–specimen distance was 500 mm. The exposed films were analyzed with a double-beam microdensitometer manufactured by Joyce, Loebl and Co., Ltd..

Results and Discussion

The results are divided into two sections, namely phase Diagrams and Morphology and Structure. In the first section we will be concerned mainly with the melting and crystallization behavior of the quasi-binary systems as studied by differential scanning calorimetry (DSC). In the second section, on the morphology and structure, attention will be focused on microscopic and X-ray studies.

Phase Diagrams. The phase diagrams or, rather, melting point/composition diagrams that will be presented in this paper were determined using DSC according to the procedure which was described extensively in an earlier paper on the phase behavior of polymeric systems.[16]

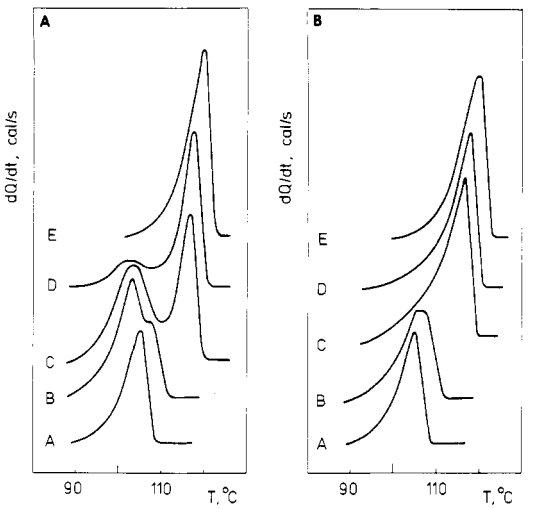

Figure 1. DSC melting thermograms of mixtures of the polyethylene fractions 1000 and 2000. Volume fraction 2000: A, 0.00; B, 0.13; C, 0.42; D, 0.80; E, 1.00. (A) Samples cooled down to solidify at 10 °C/min. (B) Samples quenched in cold water.

The System 1000/2000. This system is composed of the low molecular weight fractions designated 1000 and 2000, having molecular weights of $\bar{M}_n$ = 980 and $\bar{M}_n$ = 1790 and melting points of 105.0 and 120.5 °C, respectively. Fractions with these low molecular weights usually crystallize into fully extended chain crystals. Hence their melting temperatures will be close to the equilibrium melting points (T_m^0), which may be calculated using the relation of Flory and Vrij[17] or Broadhurst (see ref 18) for T_m^0 as a function of the molecular weight. Using the latter equation we calculated for the fractions 1000 and 2000 respectively $T_m^0(1000)$ = 106.2 °C and $T_m^0(2000)$ = 122.0 °C. The close agreement between the experimental melting points and the calculated values of the equilibrium melting temperatures is indicative of the fact that these low molecular weight fractions indeed crystallized under the present experimental conditions into fully extended chain crystals.[5]

Two sets of DSC melting thermograms of the pure fractions 1000 and 2000 and mixtures thereof covering the total range of compositions are given in Figure 1.

The melting curves presented in Figure 1A were recorded from specimens that previously were cooled down at a rate of 10 °C/min. The thermograms of the quasi-binary mixtures appeared to consist of two endotherms. The peak at the lower temperature was found to be independent of the overall composition of the mixtures and is therefore likely to be attributed to the melting of a eutectic.[16] The position of the high-temperature peak, on the contrary, depended on the concentration. The same results were obtained for mixtures that were cooled down at rates which ranged from 1.25 to 20 °C/min. A study of the influence of the heating rate on the melting behavior disclosed that both the position and the shape of the melting endotherms were independent of the scan speed. This finding evidently demonstrates that the multiple melting of the mixtures was not a result of recrystallization during the heating procedure.

A quite different melting behavior was observed if the same mixtures were cooled down to solidify more rapidly, e.g., by quenching in water that had a temperature of about 10 °C. This is illustrated in Figure 1B, where a set of melting thermograms of these quenched mixtures is

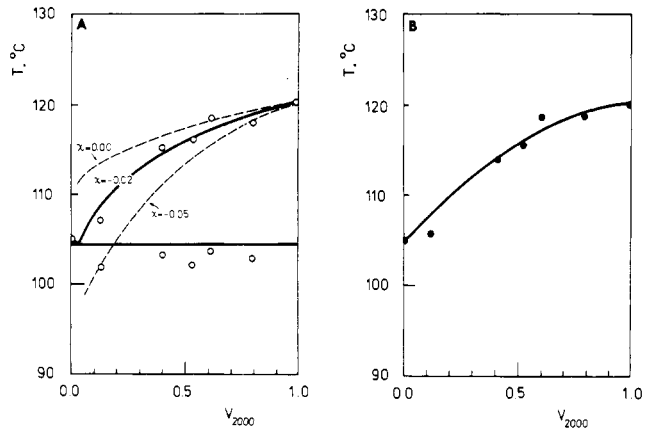

Figure 2. Melting point/composition diagrams of the quasi-binary system of the polyethylene fractions 1000 and 2000. (A) Samples cooled down at 10 °C/min. Liquidus curves calculated according to eq 1 with $\chi = 0.00$, $\chi = -0.02$, and $\chi = -0.05$. (B) Samples quenched in cold water. v_{2000} indicates volume fraction 2000.

presented. It is seen in this figure that the melting curves of all samples now exhibit only one endotherm, albeit a rather broad one in the case of the quasi-binary mixtures. The same observation was made for specimens that were quenched under milder conditions. In fact, mixtures cooled down from the melt to temperatures as high as 80 °C invariably showed one single endotherm in the DSC thermogram. Also in the case of these quenched samples the heating rate did not affect the shape and the position of the endotherms. The thermal stability of the solidified mixtures is illustrated by the fact that the melting behavior did not change after annealing the specimens at 90 °C for 120 h. Finally, attention should be drawn to the fact that the melting temperatures of the pure fractions were independent of the cooling rate. This indicates that under the present solidification conditions no chain folding was involved in the crystallization of these samples.[5] Additional evidence for this statement will be presented in the section Morphology and Structure.

The melting data that were obtained by differential scanning calorimetry were employed to construct the temperature/composition diagrams of the systems 1000/2000 under the various solidification conditions studied, as shown in Figure 2. It should be noted that the resolution of DSC curves into a solidus and liquidus is difficult and highly inaccurate. Therefore only the peak temperature assigned to the liquidus was used.

Figure 2A shows the melting points of the samples that were cooled down at a rate of 10 °C/min, prior to recording the heating curves. It is seen in this figure that under the experimental conditions employed we are dealing with a true simple eutectic behavior of the quasi-binary system 1000/2000. The eutectic point is located very close to the axis of the fraction 1000. It was shown earlier[13,15,19] that for polymeric mixtures this type of phase diagram may be described with the well-known relation for melting-point depression under thermodynamic equilibrium conditions according to Flory and Huggins:[20]

$$\frac{1}{T_{m,1}} - \frac{1}{T_{m,1}^0} = -\frac{R}{\Delta H_{u,1}}\left[\frac{1}{x_1}\ln v_1 + \left(\frac{1}{x_1} - \frac{1}{x_2}\right)v_2 + \chi v_2^2\right] \quad (1)$$

Here the subscripts 1 and 2 refer to the components 1 and 2, respectively, which are interchangable. T_m^0 is the equilibrium melting temperature and T_m is the melting point in the mixture. R is the gas constant and ΔH_u is the enthalpy of fusion per mole of structural units. The number of segments per chain molecule is denoted by x. χ is the Flory–Huggins interaction parameter, which is here defined per mole of segments. The values of the various parameters in eq 1 for the system composed of the fractions 1000 and 2000 (referred to as components 1 and 2, respectively) are $T_{m,1}^0 = 378.2$ K, $T_{m,2}^0 = 393.7$ K, $x_1 = 70$, and $x_2 = 128$. Similar to the equilibrium melting temperature, the enthalpy of fusion depends on the molecular weight. Using the relation of Flory and Vrij[17] we calculated for the fractions 1000 and 2000: $\Delta H_{u,1} = 3.68$ kJ/mol and $\Delta H_{u,2} = 3.80$ kJ/mol. The final parameter to be substituted in eq 1 is the Flory–Huggins interaction parameter. The value of χ is a matter of doubt. Values that have been reported for mixtures of n-alkanes and polyethylenes range from 0.37 for the system n-C_6H_{14}/polyethylene[21] to −1.3 for n-$C_{32}H_{66}$/polyethylene.[22] However, it now seems to be well established that χ decreases with increasing number of carbon atoms of the n-alkane, approaching a value close to zero for long chains (see, e.g., ref 21–23). The interaction parameter may depend not only on the chain length but also on the concentration and temperature. For good solvents this effect is minor, and it will therefore be neglected in the present study. As it turns out the position of liquidus given by eq 1 is rather sensitive to differences in the value of χ. This is illustrated in Figure 2A, where the melting point curve of the fraction 2000 is plotted for various values of χ. It is seen that $\chi = -0.02$ yields a good fit of the theoretical liquidus to the experimental data. The slightly negative value of the interaction parameter indicates a nearly athermal behavior of the system of low molecular weight polyethylene fractions, a fact that has also been pointed out by Asbach and Kilian.[13] Finally, the solid lines in Figure 2A represent the equilibrium phase diagram of the system 1000/2000. The Flory–Huggins theory of melting-point depression predicts a eutectic point at a volume fraction 2000 of $v_{2000} = 0.02$ and at a temperature of 104.5 °C. The experimental eutectic temperature was found to be about 2 °C lower. This may be due to the fact that the Flory–Huggins theory does not hold for very diluted systems, i.e., the region in which the eutectic point was found. Hence a difference between predicted and experimental eutectic temperature may be expected in this concentration range. Another factor involved may be the presence of small amounts of impurities giving rise to a depression of the eutectic point. However, the close agreement between the equilibrium phase diagram and the experimental melting point/composition diagram, as it can be inferred from Figure 2A, leads to the conclusion that the system 1000/2000 follows closely to the thermodynamic predictions at rates of cooling lower than 20 °C/min. It should be noted that, due to the fact that the eutectic point is located very close to the axis of the component with the lower molecular weight, one finds upon crystallizing mixtures of this system that the genuine eutectic crystallization process (i.e., the simultaneous generation of two crystalline phases) is not observed. Rather, successive crystallization of the two fractions occurs.

In Figure 2B the melting data are given for the samples that were quenched in cold water. It is seen in this figure that we are now dealing with a melting point/composition diagram of a binary system that forms solid solutions over the entire concentration range, rather than with a eutectic system. In seeking to describe this temperature/composition diagram, one has to bear in mind that there are two types of solid solutions of homologous chain molecules,

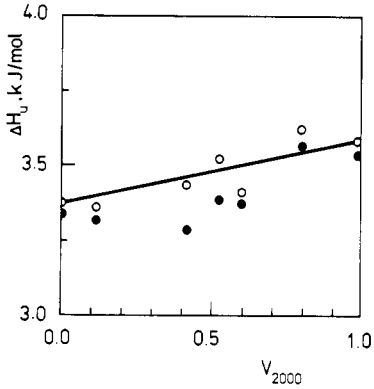

Figure 3. Heats of fusion (ΔH_u) of the system 1000/2000. (○) Samples cooled down at 10 °C/min. (●) Samples quenched in cold water. Solid line calculated with eq 2.

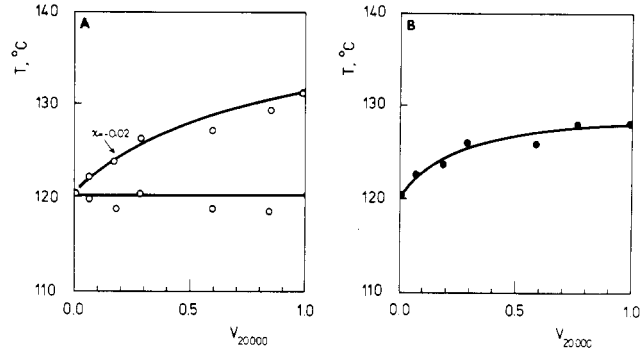

Figure 4. Melting point/composition diagrams of the quasi-binary system of the polyethylene fractions 2000 and 20000. (A) Samples cooled down at 10 °C/min. Liquidus of the fraction 20000 calculated with eq 1 with T_m^0 = 131 °C and χ = −0.02. (B) Samples quenched in cold water. v_{2000} indicates volume fraction 20000.

as was already pointed out in the introduction to this paper: first, the equilibrium solid solutions, such as for example in the systems n-$C_{19}H_{40}/n$-$C_{21}H_{44}$, n-$C_{30}H_{62}/n$-$C_{35}H_{72}$, etc.,[11-14] or in general in systems that meet the requirement $\Gamma\Delta x \leq 2$;[6] and, second, the solid solutions we are currently considering. As was shown above, the latter kind of mixed crystals may be generated from a binary melt of a eutectic system, if the rate of solidification is sufficiently high to impede the separation into two solid phases. For obvious reasons we will refer to this type of mixed-crystal system as a metastable or nonequilibrium solid solution. Theories of melting and crystallization of the first kind of solid solution have been developed by Lauritzen, Passaglia, and DiMarzio[24] and Asbach and Kilian.[13] These treatments, however, cannot be applied to describe the present system, since in melting the metastable solid solutions a true equilibrium between the solid and liquid state does not exist at any instant. Moreover, the molecular structure of equilibrium and nonequilibrium solid solutions may differ substantially, as will be seen in the section Morphology and Structure. At present the problem outlined above has not been solved.

Enthalpies of fusion of the various samples of the quasi-binary system 1000/2000 were calculated in the usual way from the DSC melting thermograms. The results are displayed graphically in the form of the enthalpy of fusion/composition diagram shown in Figure 3. As is customary the enthalpy is expressed per mole of CH_2 segments and designated ΔH_u. The open circles in this figure indicate the data that were obtained for the specimens cooled down at 10 °C/min. In this case the enthalpy of fusion of a given quasi-binary mixture was calculated from the total peak area in the thermogram, composed of two endotherms, and it therefore represents an overall ΔH_u. The solid points in the graph of Figure 3 denote the enthalpies of fusion of the samples that were quenched in cold water. ΔH_u of the slowly cooled fraction 1000 amounts to 3.37 kJ/mol. This corresponds to a crystallinity of 92%, if based on an equilibrium value of ΔH_u = 3.68 kJ/mol for a fraction with a molecular weight (mol wt) of 980, calculated according to Flory and Vrij.[17] The enthalpy of fusion of the pure fraction 2000, solidified under the same conditions, was 3.60 kJ/mol units. Calculating ΔH_u = 3.80 kJ/mol for 100% crystalline polyethylene with mol wt = 1790,[17] the crystallinity of the slowly cooled fraction 2000 was 95%. It can be inferred from Figure 3 that the overall enthalpy of fusion of the mixtures that were cooled down slowly is described reasonably well by the relation:

$$\Delta H_u(\text{mixture}) = (1 - v_{2000})\Delta H_u(1000) + v_{2000}\Delta H_u(2000) \quad (2)$$

as was expected. It is of interest to note that the enthalpies of fusion of the quenched samples are but slightly lower than those of the slowly cooled specimens, on the average only 0.08 kJ/mol, which corresponds to a decrease in crystallinity by about 2%. Apparently, the rapid crystallization that forced the molecules of both fractions into a common crystalline lattice to form solid solutions did not cause a large decrease in crystallinity. This observation is especially important in regard to the structure of the nonequilibrium solid solutions which will be dealt with in a following section.

The System 2000/20000. The fractions 2000 and 20000 constitute the next quasi-binary system to be discussed. The 20000 fraction has a number average molecular weight of 20 × 10^3 that exceeds by far the upper limit of roughly 10 × 10^3 (depending on kinetic factors) for fully extended chain crystallization under ambient conditions (see, e.g., ref 1 and 25). According to the equation of Broadhurst,[18] polyethylene with a molecular weight of 20 × 10^3 has an equilibrium melting temperature (i.e., the melting point of infinitely large extended chain crystals) of 143.7 °C. The experimental melting temperatures of the fraction 20000 in the present study ranged from 127.5 to 131.5 °C for samples quenched in cold water and cooled down from the melt at 1.25 °C/min, respectively. The difference between the equilibrium and experimental melting points is well known to be mainly due to the limited crystallite size, especially in the chain-axis direction, in the polymeric solid.

Despite the fact that the fraction 20000 displayed the rather complex crystallization behavior typical of high polymers, the system 2000/20000 was found to act in a very similar way to mixtures of the fractions 1000 and 2000. Here also fractionation occurred during solidification at cooling rates lower than 20 °C/min, as could be inferred from the appearance of two endotherms in the melting thermograms of these slowly cooled samples. Quenching of the molten mixtures to temperatures lower than 80 °C induced the formation of mixed crystals, giving rise to one single melting endotherm. The melting temperature/composition diagrams of the system 2000/20000, that were constructed with the DSC melting data, are presented in Figure 4.

The melting points of samples that were cooled down at a rate of 10 °C/min prior to recording the melting thermograms are given in Figure 4A. It is seen in this figure that the quasi-binary system 2000/20000 behaves at low solidification rates as a simple eutectic system. The eutectic point is located almost at the axis of the fraction 2000. In attempting to describe this experimental phase diagram using eq 1, it has to be borne in mind that this

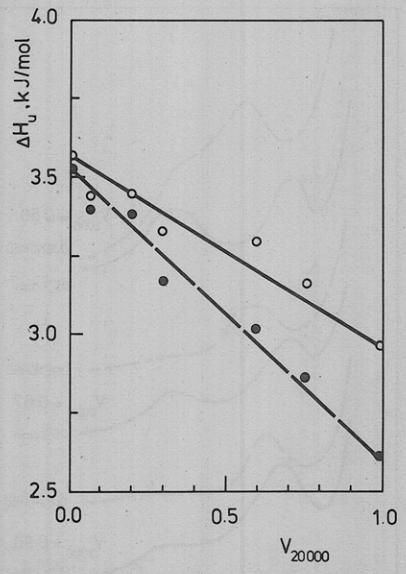

Figure 5. Heats of fusion (ΔH_u) of the system 2000/20000. (○) Samples cooled down at 10 °C/min. (●) Samples quenched in cold water. Curves calculated similar to eq 2.

relation for the melting point depression only holds for thermodynamic equilibrium conditions, i.e., circumstances where the polymer forms infinite large fully extended chain crystals. It was shown above that under the present solidification conditions the fraction 20000 crystallized into metastable solid states, rather than equilibrium crystals. The melting temperature of this crystalline phase deviates markedly from the equilibrium melting point, which is presumably due to the limited crystallite size and the presence of lattice defects, cilia, etc. in the polymeric solid. The limited size of the crystallites may be taken into account using the Gibbs–Thomson equation.[26] A rigorous treatment of the effect of the crystal thickness and the amorphous fraction on the melting temperature, based on the fringed micelle concept, was given by Flory.[27] However, the internal defects, the limited transverse dimension of the crystallites, etc. must still be accounted for in a treatment of the melting point depression of metastable polymeric solids; at present such a theory is not available. It turned out in this study that the experimental phase diagram of the system 2000/20000 could be very well described with eq 1, if the actual melting temperature of the fraction 20000 (404.7 K) was substituted, rather than the equilibrium melting point T_m^0 of a polyethylene fraction with a molecular weight of 20×10^3. The result of the calculations according to this semiemperical method, that was also used by Nakajma and Hamada,[21] is represented in Figure 4A. The enthalpy of fusion of the fraction 20000 had a value of 3.95 kJ/mol units, and the number of segments x was 1426. The optimum χ value was established to be −0.02, which was the same in the system 1000/2000.

In Figure 4B the melting points are given from mixtures of the system 2000/20000 that were solidified from the melt by quenching in cold water. Evidently, mixed crystals form under these crystallization conditions over the entire concentration range and fractionation does not occur.

The enthalpies of fusion of the specimens crystallized under the various conditions are presented in Figure 5. Once more we observed that the heat of fusion of a mixture of polyethylene fractions is linearly related to the concentration both for solid solutions and separate solid phases. The fact that the ΔH_u values of the present solid solutions are lower than those of the fractionated mixtures is predominantly due to the decrease in enthalpy of fusion

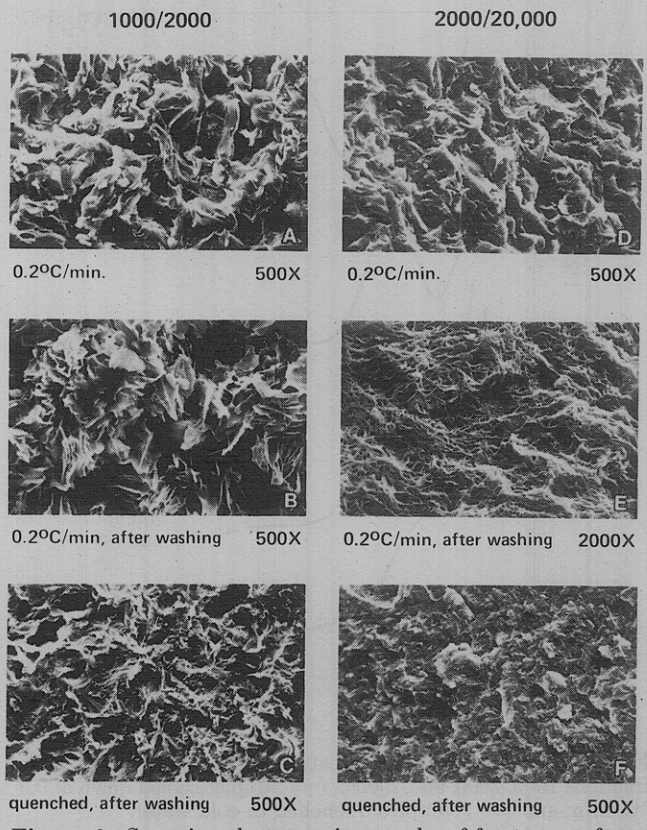

Figure 6. Scanning electron micrographs of fracture surfaces of mixtures of the systems 1000/2000 (A, B, C; volume fraction 1000 is 0.40) and 2000/20000 (D, E, F; volume fraction 2000 is 0.28). Samples A, B, D, and E were cooled down at 0.2 °C/min, and samples C and F were quenched in cold water. Surfaces B and C were washed with hot *p*-xylene at 89 °C during 1 min, and E and F were washed with hot *p*-xylene at 93 °C.

of the fraction 20000 upon rapid crystallization, and it is not caused by the particular process of solid solution formation. ΔH_u of the slowly cooled 20000 fraction was 2.95 kJ/mol, which corresponds to a crystallinity of 75%, if based on the value 3.95 kJ/mol units of 100% crystalline polyethylene with a molecular weight of 20×10^3.[17] For the cold water quenched sample we established the enthalpy of fusion to be 2.62 kJ/mol units; this indicates a drop in the crystallinity by 9% upon quenching.

Morphology and Structure. This section deals with some morphological and structural characteristics of the metastable solid solutions of the systems 1000/2000 and 2000/20000 and of the composite polymeric solids comprising the two separate phases.

In studying the crystallization behavior of the quasi-binary mixtures of polyethylene fractions in the optical microscope (equipped with a temperature regulated hot stage, Mettler FP52), it was observed that consecutive crystallization of the two fractions occurred during slow cooling. In the system 1000/2000 at first coarse axialites of the fraction 2000 were generated from the melt, and subsequently the remaining liquid solidified. By contrast with this rather step-wise solidification process, simultaneous crystallization of the two fractions into small well-defined spherulites was observed upon quenching the binary melts to room temperature. The system 2000/20000 was found to behave in a very similar way under the various solidification circumstances. It should be noted that the present observations are essentially similar to those made by Keith and Padden in their extensive studies on the morphology of polymer crystals (see, e.g., ref 28).

Scanning electron micrographs of fracture surfaces of some of the quasi-binary mixtures are shown in Figure 6.

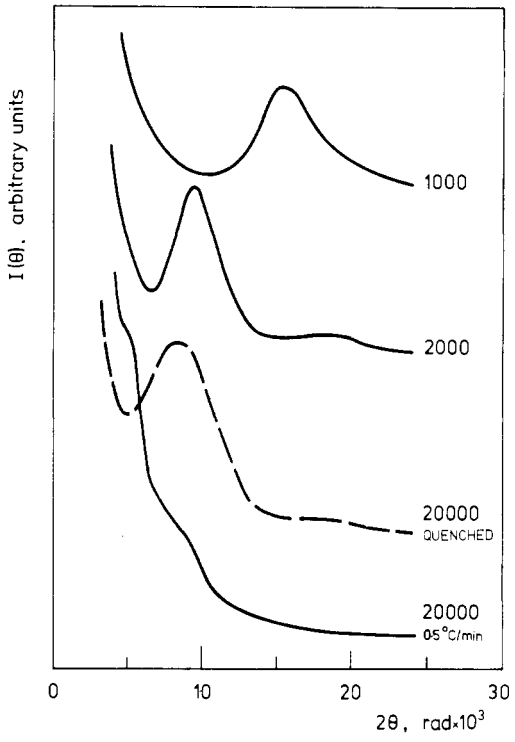

Figure 7. Small-angle X-ray scattering curves of polyethylene fractions 1000, 2000, and 20000: (—) samples cooled down at 0.5 °C/min; and (- - -) samples quenched in cold water.

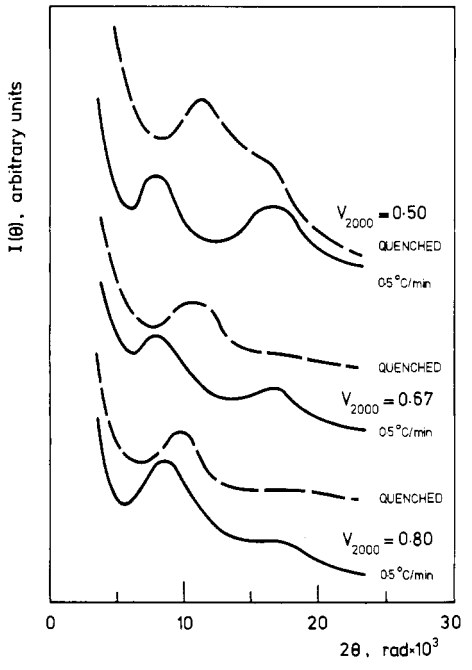

Figure 8. Small-angle X-ray scattering curves of mixtures of the system 1000/2000. Volume fractions 2000 are 0.50, 0.67 and 0.80: (—) samples cooled down at 0.5 °C/min; and (- - -) samples quenched in cold water.

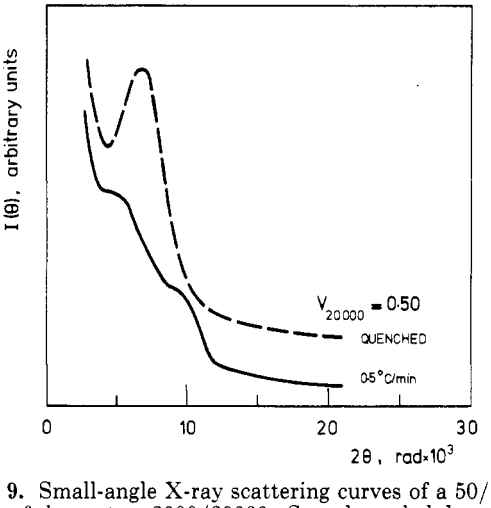

Figure 9. Small-angle X-ray scattering curves of a 50/50 v/v mixture of the system 2000/20000. Sample cooled down at 0.5 °C/min (—) and quenched in cold water (- - -).

The photomicrographs A, B, and C were taken from mixtures of the system 1000/2000 that contained 40% by volume of the fraction 1000. Figure 6D,E,F displays structures of mixtures of the system 2000/20000. The volume fraction 2000 was 0.28. The fracture surfaces shown in Figures 6A and 6D were obtained by breaking samples that were cooled down from the melt at a rate of 0.2 °C/min, i.e., at a cooling rate where fractionation occurred. As is illustrated by these figures, a coarse spherulitic structure was formed. The low molecular weight fractions could partially be removed from these fracture surfaces without destroying the overall microstructures leaving a highly porous polymeric material. Examples of the remaining morphology are shown in Figures 6B and 6E; these surfaces were treated for 1 min with hot *p*-xylene at 88 and 93 °C, respectively, and subsequently washed with acetone. Because of the dissolution of the 2000 fraction the coarse structure of the spherulites of the high molecular component appears more pronounced.

A quite different morphology was observed for specimens cooled down from the melt so quickly that mixed crystal formation was induced. The electron photomicrographs shown in Figures 6C and 6F were taken from fracture surfaces of samples that were cooled down by quenching in cold water and then treated with hot *p*-xylene. It can be seen that a fine homogeneous microstructure had developed. Treatment with hot *p*-xylene at 93 °C did not affect the morphology of these specimens. This observation supports the conclusion that mixed crystal formation occurs during rapid crystallization.

Wide- and small-angle X-ray studies were carried out in an effort to obtain information on the molecular arrangement of the chains in the solid solutions and the fractionated solids. Examination of the diffraction patterns at wide angles revealed that all samples (pure fractions, slowly cooled and quenched mixtures) invariably showed, among others, the 110 and 200 reflections at an angle of 21.6 and 24.0°, respectively, that are so characteristic of the orthorhombic polyethylene crystal structure.[29]

The X-ray scattering curves in the low-angle region of the pure fractions and mixtures thereof are presented in Figures 7, 8, and 9.

At first we will confine our attention to the system 1000/2000. The SAXS curve of the pure low molecular weight fraction 1000 exhibits a distinct maximum (Figure 7) at an angle that can readily be related to the long period in the lamellar structure of fully extended chain crystals of this polyethylene sample. After application of the Lorentz and polarization corrections to the scattering curve,[30] the angular position of the maximum displacement of the recorded curve from an assumed smooth diffuse scatter background was determined. Subsequently, the long period was calculated, using Bragg's law, to be 10.5 nm for the slowly cooled fraction 1000. The end-to-end distance of a polyethylene molecule with a molecular weight of 980, in the all-trans conformation, is 9.0 nm. The long period in the quenched fraction 1000 was established

Table II
Small-Angle X-ray Spacings in the System 1000/2000

	long period, nm	
v_{2000}	cooled at 0.5 °C/min	quenched
0.00	10.5	10.1
0.50	9.5, 18.8	13.6
0.67	9.2, 18.4	14.8
0.80	9.8, 18.0	16.1
1.00	17.9	17.3

to be 10.1 nm (see Table II), which is only slightly lower than in the slowly cooled specimen. Clearly, no chain folding was involved in the rapid crystallization of this fraction. The SAXS curve of the fraction 2000, also shown in Figure 7, displayed one pronounced maximum and a second rather weak peak at diffraction angles in the ratio 1:2.03. This second maximum is therefore very likely to be attributed to the second-order reflection. The long period in the slowly cooled sample amounted to 17.9 nm and to 17.3 nm in the quenched specimen. The end-to-end distance of a polyethylene zig-zag chain with a molecular weight of 1790 is 16.3 nm. From the X-ray studies we have to conclude that the 2000 fraction also crystallized into fully extended chain crystals, confirming conclusions obtained earlier in the calorimetric investigations.

Small-angle X-ray scattering curves of various blends of the fractions 1000 and 2000 are presented in Figure 8. In this figure the solid lines represent the curves of samples that were cooled down from the melt at a rate of 0.5 °C/min, thus at a rate where fractionation occurred during the solidification process. The interrupted curves correspond to mixtures that were quenched in cold water. It is seen in Figure 8 that the SAXS curves of the slowly cooled specimens invariably showed two peaks at diffraction angles that are independent of the overall concentration of the mixtures. By contrast, the relative intensity of the two maxima depended on the amount of each fraction in the blends. The long periods, corresponding to the angular positions of the peaks, are given in Table II. It can be inferred from this table that the long spacings in the quasi-binary mixtures are in close agreement with those of the pure fractions. This observation justifies the conclusion arrived at in the previous section that at these low solidification rates fractionation occurred during crystallization.

Quite different SAXS curves were recorded for mixtures of the system 1000/2000 that were quenched in cold water (see Figure 8). In this case the scattering curves consisted of one pronounced, frequently rather broad, peak at a diffraction angle that depended on the composition of the mixtures. In addition, a weak reflection was observed at wider angles. The long spacings calculated from the angular positions of the major peaks in the SAXS curves are listed in Table II. Clearly, the "new" X-ray period is intermediate in length between the long spacings of the two fractions 1000 and 2000 and increases with increasing concentration of the fraction 2000. In seeking to describe the relation between the long period of the solid solutions and composition, we found that there is not a straightforward linear dependence, as suggested by Vegard's law of additivity.[31] This law states that in a binary system forming a continuous series of solid solutions the lattice parameters are linearly related to the concentration of one of the components. The experimental X-ray spacings invariably exceed the values based on additive behavior. The origin of the weak reflections at angles corresponding to long periods of 9.6, 8.5, and 8.3 nm in the SAXS curves of mixtures with a volume fraction 2000 of 0.50, 0.67, and 0.80, respectively, is somewhat obscure. In most cases the ratio of the diffraction angles of the weak and dominant peaks differs substantially from 2. Therefore, the second reflection is not likely to be a second-order maximum. Rather it may be attributed to the presence of small amounts of crystals of the pure 1000 fraction in the quenched samples. This would then indicate that dispite the rapid solidification process some fractionation still occurred during the crystallization; however, this is not supported by the calorimetric measurements.

Table III
Small-Angle X-ray Spacings in the System 2000/20000

	long period, nm	
v_{20000}	cooled at 0.5 °C/min	quenched
0.00	17.9	17.3
0.50	15.9, 25.1	20.8
1.00	17.4, 28.5	18.5

It should be noted that the present observations in the X-ray studies are not uniquely restricted to the system composed of the polyethylene fractions 1000 and 2000. In fact, rather similar results were obtained in X-ray studies on mixtures of homologous dioligourethanes,[32] fatty acids,[33] soaps,[34] paraffins (e.g., ref 12, 13, and 35), and blends of ethylene/vinyl acetate copolymers and paraffin wax.[36] The SAXS patterns of mixtures of components with a substantial difference in chain length displayed diffraction maxima that corresponded to the long periods of the pure constituents. In mixtures that solidify to form equilibrium solid solutions, e.g., n-$C_{29}H_{60}$/n-$C_{31}H_{64}$, a new composition dependent long spacing was found in the X-ray scattering curves at low angles. This new period was intermediate in length between those of the pure components but exceeded the value based on additive behavior.[12]

Next we will discuss the system 2000/20000. The small-angle X-ray scattering curves of the fraction 20000, both of the slowly cooled and quenched specimens, are given in Figure 7. Unlike those of the low molecular weight samples the SAXS curve of this polyethylene fraction strongly depended on the crystallization conditions, as is typical of high polymers (e.g., ref 37 and 38). Two diffraction maxima were observed in the curve of the specimen that was cooled down from the melt at 0.5 °C/min. The corresponding long spacings were calculated to be 17.4 and 28.5 nm (see Table III). The scattering curve of the quenched material displayed only one, rather sharp, diffraction peak at an angular position that was related to a long spacing of 18.5 nm. The present X-ray results are in close agreement with reported data of polyethylene samples with similar molecular weights, solidified under comparable conditions.[18,37,38] The origin of the two long periods in the slowly cooled specimens has long been obscure. According to Kortleve and Vonk the maximum at the larger angles is simply a second-order reflection.[38] Hoffman et al. postulated on the other hand that the longer period corresponds to the aged stage of the initial structure that is characterized by the smaller spacing.[18]

The SAXS curves of a 50/50 v/v mixture of the fractions 2000 and 20000 are presented in Figure 9, and the long periods that were calculated from the angular positions of the diffraction maxima are listed in Table III. The scattering curve of the slowly cooled mixture displayed two peaks that can readily be related to the diffraction peaks of the pure components. The quenched mixture was characterized by just one sharp maximum in the SAXS curve. Unexpectedly and unlike the results obtained for

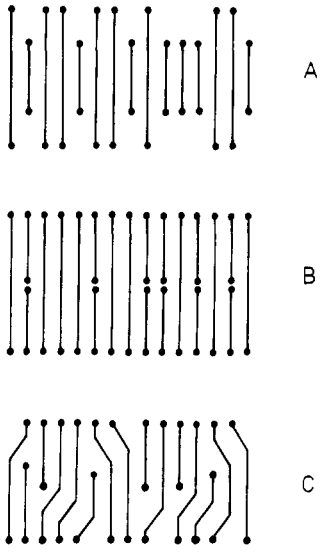

Figure 10. Various schematic representations of the structure of solid solutions in the system 1000/2000.

solid solutions of the system 1000/2000, the long period in this quenched sample exceeded those in the pure constituents. This interesting phenomenon, which is due to the simultaneous or, rather, coupled crystallization of long and short chains into solid solutions, definitely urges further investigation.

Since it is very difficult to arrive at a decisive conclusion concerning the structure of the separate solids and solid solutions purely from X-ray scattering data, additional density measurements were carried out on the various samples. The main issue is, of course, whether or not the mixtures have a different, most likely a lower, density than the pure fractions. The densities of the fractions 1000 and 2000 were established to be 0.99 g/cm^3 irrespective of the solidification conditions. The slowly cooled mixtures 1000/2000 had the same density, while those of the solid solutions were lower by only 2%. Very similar results were obtained for the system 2000/20000. The slowly cooled 20000 fraction had a density of 0.97 g/cm^3, and the quenched sample had a density of 0.96 g/cm^3. The densities of the 50/50 v/v mixture 2000/20000 were measured to be 0.98 and 0.97 g/cm^3 for the slowly cooled and quenched specimens, respectively.

Concluding Remarks

In this section we will summarize the results of this study on the structure and properties of the solid solutions that are generated from a heterodisperse melt upon rapid cooling and of the composite solids produced at the low solidification rates where fractionation occurred.

The present investigation confirms the classical picture of separate solid phases in fractionated polymer samples. In our binary model systems two solids formed consecutively from the melt upon slow cooling to give solid mixtures with a simple eutectic-type melting point/composition diagram. The mixtures of the polyethylene fractions were found to behave nearly athermally, as is indicated by the value of the Flory–Huggins interaction parameter $\chi = -0.02$ in the description of the experimental phase diagram. The structure of the separate solids is simply a blend of closely packed lamellae of the pure constituents, which is inferred from the density and the multiple reflections in the SAXS diagrams. Finally, the enthalpies of fusion of the mixtures obeyed the law of additivity.

Upon quenching the binary melts the polyethylene fractions crystallized into a continuous series of mixed crystals. These metastable solid solutions exhibited a melting range, which is characteristic of this type of crystal, rather than the separate melting points of the slowly cooled mixtures. The enthalpies of fusion of the mixed crystals were found to be linearly related to the concentration of one of the components. The densities of the solid solutions, which were only slightly lower than that of the separate solids, indicate that their structure is closely packed. At this point it may be useful to recall a recent study on phase transitions of *n*-alkane systems by Bonsor and Bloor.[14] These authors reported that equilibrium solid solutions of the system n-$C_{21}H_{44}/n$-$C_{23}H_{48}$ have densities that were up to 2% lower than those of pure constituents. This is caused by the vacancies in the solid solution structure of randomly stacked molecules due to the difference in chain length. If the structure of the metastable solid solutions we are currently dealing with would be the same as the arrangement of the molecules in the equilibrium mixed crystals, the densities of, e.g., quenched mixtures of the system 1000/2000 would be substantially lower than the observed value of 0.97 g/cm^3, considering the large difference in chain length of the molecules (see Figure 10A). A solid solution model where two molecules of the fraction 1000 occupy the site of one 2000-fraction molecule (Figure 10B) seems unlikely in view of the "new" SAXS-lamellar spacing of the solid solutions and its concentration dependence. This composition relation may be explained by the solid solution model presented in Figure 10C and, in fact, provides strong support for it. The schematic representations of the nonequilibrium solid solutions of the system 1000/2000 in Figure 10 are, of course, oversimplified. The molecules may very well be inclined to yield oblique layers.[39] Moreover the mixed crystals are likely to have a multilayer nature.

The structure of the metastable solid solutions that comprise both fully extended and nonextended chains, such as in the system 2000/20000, is much more obscure, in particular since the molecular arrangement in high polymeric solids is still a controversial matter (see, e.g., 40). Hence it will remain a topic to be studied in the future.

Acknowledgment. The financial assistance of the National Research Council of Canada is gratefully acknowledged. One of us (P.S.) wishes to thank the Dutch State Mines/DSM, Geleen, The Netherlands, for a leave of absence.

References and Notes

(1) F. R. Anderson, *J. Appl. Phys.*, **35**, 64 (1964).
(2) P. H. Geil, F. R. Anderson, B. Wunderlich, and T. Arakawa, *J. Polym. Sci., Part A-2*, **2**, 3707 (1964).
(3) T. Kawai and A. Keller, *J. Polym. Sci., Part B*, **2**, 333 (1964).
(4) A. J. Pennings, *Proc. Conf. Charact. Macromol. Struct.*, 214 (1964).
(5) B. Wunderlich, "Macromolecular Physics", Vol. 2, Academic Press, New York, 1976, p 91.
(6) P. Smith and R. St. John Manley, *Macromolecules*, in press.
(7) C. W. Bunn, A. J. Cobbold, and R. P. Palmer, *J. Polym. Sci.*, **28**, 365 (1958).
(8) A. Mehta and B. Wunderlich, *Colloid. Polym. Sci.*, **253**, 193 (1975).
(9) D. M. Sadler, *J. Polym. Sci., Part A-2*, **9**, 779 (1971).
(10) J. L. Kardos, H.-M. Li, and K. A. Huckshold, *J. Polym. Sci., Part A-2*, **9**, 2061 (1971).
(11) W. M. Mazee, *J. Inst. Pet., London*, **35**, 97 (1949).
(12) Yu. V. Mnyukh, *J. Struct. Chem. (Engl. Transl.)*, 1, 346 (1960).
(13) G. I. Asbach and H. G. Kilian, *Ber. Bunsenges. Phys. Chem.*, **74**, 814 (1970).
(14) D. H. Bonsor and D. Bloor, *J. Mater. Sci.*, **12**, 1559 (1977).
(15) P. Smith and R. St. John Manley, paper presented at the International Symposium on Flow-Induced Crystallization, Midland, Mich., 1977.
(16) P. Smith and A. J. Pennings, *Polymer*, **15**, 413 (1974).

(17) P. J. Flory and A. Vrij, *J. Am. Chem. Soc.*, **85**, 3548 (1963).
(18) J. D. Hoffman, L. J. Frolen, G. S. Ross, and J. I. Lauritzen, Jr., *J. Res. Natl. Bur. Stand., Sect. A*, **79**, 671 (1975).
(19) R. B. Prime and B. Wunderlich, *J. Polym. Sci., Part A-2*, **7**, 2061 (1969).
(20) P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, 1953, p 568.
(21) A. Nakajima and F. Hamada, *Kolloid Z. Z. Polym.*, **205**, 55 (1966).
(22) B. Ke, *J. Polym. Sci.*, **50**, 79 (1961).
(23) P. J. Flory, A. Ciferri, and R. Chiang, *J. Am. Chem. Soc.*, **83**, 1023 (1961).
(24) J. I. Lauritzen, Jr., E. Passaglia, and E. A. Di Marzio, *J. Chem. Phys.*, **45**, 4444 (1966).
(25) G. I. Asbach, H. G. Kilian, and F. H. Muller, *J. Polym. Sci., Part C*, **18**, 133 (1967).
(26) W. J. Dunning in "Nucleation", A. C. Zettlemoyer, Ed., Marcel Dekker, New York, 1969, p 7.
(27) P. J. Flory, *J. Chem. Phys.*, **17**, 223 (1949).
(28) H. D. Keith, *J. Polym. Sci., Part A*, **2**, 4339 (1964).
(29) P. Zugenmaier and H.-J. Cantow, *Kolloid Z. Z. Polym.*, **230**, 229 (1969).
(30) L. E. Alexander, "X-ray Diffraction Methods in Polymer Science", Wiley, New York, 1969, p 40.
(31) G. L. Clark, "Applied X-rays", 4th ed., McGraw-Hill, New York, 1955, p 558.
(32) W. Kern, J. Davidovits, K. J. Rauterkus, and G. F. Schmidt, *Makromol. Chem.*, **43**, 106 (1961).
(33) E. Ott and F. B. Slagle, *J. Phys. Chem.*, **37**, 257 (1933).
(34) K. Hess and H. Kiessig, *Chem. Ber.*, **81**, 327 (1948).
(35) B. Belbeoch and A. Guinier, *C. R. Hebd. Seances Acad. Sci.*, **247**, 310 (1958).
(36) J. P. Tordella and P. F. Dunion, *J. Polym. Sci., Part A-2*, **8**, 81 (1970).
(37) P. H. Geil, *J. Polym. Sci., Part C*, **13**, 149 (1966).
(38) G. Kortleve and C. G. Vonk, *Kolloid Z. Z. Polym.*, **225**, 124 (1968).
(39) G. Strobl, B. Ewen, E. W. Fischer, and W. Piesczek, *J. Chem. Phys.*, **61**, 5257 (1974).
(40) P. J. Flory and D. Y. Yoon, *Nature (London)*, **272**, 226 (1978).

Molecular Fracture in Poly(chloroprene)

W. T. Mead*

Department of Materials, Queen Mary College, University of London, England.
Received August 11, 1978

ABSTRACT: Electron spin resonance spectra are reported from free-radical formation in poly(chloroprene), uniaxially deformed below T_g. Radicals formed following tensile testing are assigned to the allylic species produced by main-chain fractures $-CH_2C(Cl)=CH\dot{C}H_2$ and $-CH_2CH=C(Cl)\dot{C}H_2$. In the presence of oxygen as the test environment the allyl radicals react to produce a peroxy radical species. Similar ESR spectra were produced by UV irradiation. The effect of zinc oxide acting as cross-linking agent did not complicate the ESR spectra, although spectra from dicumyl peroxide cross-linked poly(chloroprene) were assigned to oxidative radical products. The decay of the allyl radicals with temperature is studied.

The electron spin resonance (ESR) spectrum of free radicals produced in uniaxially deformed poly(chloroprene) has not been published previously. Radicals produced by photolysis of poly(chloroprene) have been reported.[1] The ESR spectrum was a broad singlet and no identification of the radical specimens was given. Radicals have recently been detected in ultraviolet irradiated poly(chloroprene)[2,3] (CR) although the assignment was tentative since only a broad first derivative ESR spectrum was obtained and even the second derivative spectrum showed only traces of hyperfine structure. Assignment was not conclusive for interpretation without support of ESR spectra of allylic radicals from other polydienes.[4,5] A peroxy radical species was observed during uniaxial deformation of poly(chloroprene).[6,7] This communication reports radicals produced by tensile deformation of cross-linked poly(chloroprene) using both zinc oxide and dicumyl peroxide as the cross-linking agents. Further, no ESR study of the oxidation of poly(chloroprene) has been published although it has been reported that poly(chloroprene) is more resistant to oxidation than other dienes such as polybutadiene (BR) and polyisoprene (IR).[8] An ESR study of oxidation of BR and IR has already been reported.[9,10] Radicals formed during uniaxial deformation of BR and IR at temperatures below their respective T_g's were tentatively assigned to allyl radicals possibly formed by homolytic cleavage of the weakest bond in the main chain (i.e., midway between the α- methylene bonds), and this would suggest that allyl radicals may be formed during low-temperature deformation of CR.[10]

* Address correspondence to the author at Aylesbury, HP179DA, Buckinghamshire, England.

Experimental Section

The poly(chloroprenes) used in this study were not purified. The structural units in the Neoprene W (DuPont Ltd.) used for ESR studies consisted of approximately 85% trans-1,4, 10% cis-1,4, 1.5% 1,2, and 1.0% of 3,4 addition. Neoprene W was used for the ESR studies, since unlike Neoprene WX and Neoprene G it contained no stabilizer, sulfur, vulcanization disulfide, or other compounds capable of decomposing and producing a vulcanization accelerator and hence complicating the resulting ESR spectrum. For example, Neoprene WX gave on deformation only a broad singlet ESR spectrum with no trace of hyperfine structure. The "G" type of Neoprene gave only a singlet-like spectrum which was possibly the result of inclusion of stabilizers. Samples were also irradiated in evacuated spectrosil tubes with a Phillips UV lamp.

The experimental details of the tensile testing and ESR equipment have been described more fully elsewhere.[9] The specimen was extended at room temperature prior to the low-temperature deformation, since it has been shown that the use of pretest deformation in the rubber-like state induces ductility in the elastomers at low temperature.[9] The resulting morphologies which are obtained in poly(chloroprene) by preorienting the sample prior to cooling and deforming the sample have been described by Andrews and Reeve.[11,12] The specimens were then stretched in liquid nitrogen.

A range of mechanical behavior was observed during low-temperature deformation of poly(chloroprene), and the behavior was dependent on the rate of strain, the degree of cooling, the cross-link density, and the degree of pretest deformation. The modes of deformation observed were crazing, shear yielding, and a region of ductile behavior at high pretest deformation, in which

0024-9297/79/2212-0491$01.00/0