Disruption of Crystallites by Mechanical Grinding of Poly(vinyl chloride) Resins

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ABSTRACT: PVC resins were ball milled into micron size particles. The as-polymerized and ball-milled resins were annealed at 120 °C. The enthalpies, as determined by solution microcalorimetry at 37 °C, are identical for the unmilled resins. For the ball-milled resin, an enthalpy increase of 25% occurred. Annealing the ball-milled resin resulted in enthalpy decrease from 7.2 to 5 cal/g which is 0.8 cal/g lower than the aspolymerized material, but particle size remained unchanged. X-ray studies indicate identical discrete scattering for the unmilled resins, loss of discrete scattering in the ball-milled sample, and recovery and enhancement of discrete scattering for the ball-milled–annealed sample.

There are two aspects of the physical structure of poly(vinyl chloride) that have attracted considerable amounts of research over the past few decades. These include the crystalline structure in the low-crystalline polymer and more recently studies on the particulate nature of resins and melts. Both of these are strongly suspected as being directly related to the unique properties and thus commercial importance of PVC, as well as the difficulty in processing and establishing a reliable melt–flow relationship.[1,2] The crystallinity was suggested originally from creep tests of Leaderman,[3] relaxation studies of Alfrey,[4] X-ray studies on oriented samples by Stein,[5] and melt viscosity studies of Collins,[6] to name a few. Single crystals of PVC were first reported by Smith and Wilkes[7] for very low molecular weight syndiotactic PVC and crystallinity in commercial PVC was studied by numerous authors.[8–11]

The particulate nature of PVC, i.e., that in most circumstances molecules do not act independently but as groups of molecules or aggregates, has been observed and studied in solution, in the melt, and in the solid state. In solution, the presence of aggregates has been established by methods ranging from light scattering to solution viscosities and molecular weight studies.[12–16] In the melt, this particulate nature was studied by Pezzin,[1,17] Berens and Folt,[18] Hoffman and Choi,[19] and Collins and Daniels.[20] The most complete work on the particulate morphology of solid PVC samples was done recently by Geil and coworkers[21,22] on samples processed under various conditions and plasticized to various extents. Thus the existence of crystallinity in PVC is well established as well as the presence of molecular aggregates in solutions and in the melt. The question which remains, and to which we wish to address ourselves in this paper, is in regard to the relationship, if any, between the molecular aggregates and the crystallinity. At present, most models tying the two together are purely speculative and are based solely on circumstantial evidence. This crystallinity has been suggested by many as being the mechanism tying the molecules together in the aggregates observed in solution,[12–16] and in one case a model was proposed[23] based upon an observed relationship between the disappearance of aggregates and the speculated melting temperature of crystallites under shear. It was also found that association was more likely to occur in samples polymerized at low temperature,[14] a procedure which increases the syndiotacticity in a chain and thus the crystallinity and suggests that the crystallites are indeed associated with the aggregates in solution. Further, Berens, and Folt[18] concluded from studies on die swell for PVC that increasing die swell with increasing shear rate behavior could be explained by a transition from particulate to molecular flow which may be explained as a fusion of crystallinity associated with the disappearance of the particulate nature, i.e., that crystallinity is important to the integrity of the particles. Additional evidence exists which concludes that in the solid the crystallinity acts as physical cross-links forming a continuous network of PVC molecules.[3–5] The best example of the network structure is of course the ability of PVC to be plasticized to levels as high as 90% or greater. Thus it appears that the crystallinity or order must exist both inside and between the particles which are observed as well as in the solid and plasticized states.[21,22] However, the existence of crystallites within the particles has not been observed directly and is disputed by some.[24]

In this article we will present evidence that in the aspolymerized material the resin particles or grains are constructed of much smaller particles (0.5–2 μm) bound together by crystallites. These interparticle crystallites have basically the same morphology as syndiotactic single crystals but are readily solubilized in common PVC solvents.

In this article we will attempt to follow as nearly as possible the suggested terminology of Geil[25] to describe the particulate morphology of PVC. However, in instances, the distinction between particles or particle sizes may not be so clear-cut.

Experimental Section

Materials and Sample Preparation. The sample used for the study was a suspension polymerized Geon 92 resin, provided by Dr. E. A. Collins of B. F. Goodrich. The specimens were in four forms: (a) as received, (b) ball milled for 2 weeks, (c) as received and annealed at 120 °C for 1 h, and (d) ball milled and annealed at 120 °C for 1 h. They were all in the form of powders, and the annealed powders appeared very slightly pinkish.

The samples were ball milled at room temperature in a standard size 00 porcelain ball mill at a rate of 10 rpm using grinding pebbles approximately 0.5 in. in diameter. No significant heating occurred to the samples during this very low shear grinding process.

The solvent used in the heat of solution measurements was a triply distilled cyclohexanone.

Procedures. A. Enthalpy Measurements (Solution Microcalorimetry). The experimental procedures are adequately described in the literature[26,27] and will not be described again here except to point out that all these measurements were performed at a single temperature of 37 °C.

B. X-ray Diffractometry. Two kinds of wide-angle scattering techniques were employed: a Debye–Scherrer powder diffraction and the reflection diffractometry.

1. Debye–Scherrer Powder Pattern. The Cu Kα X-ray beam was generated with a Philips Norelco generator (type

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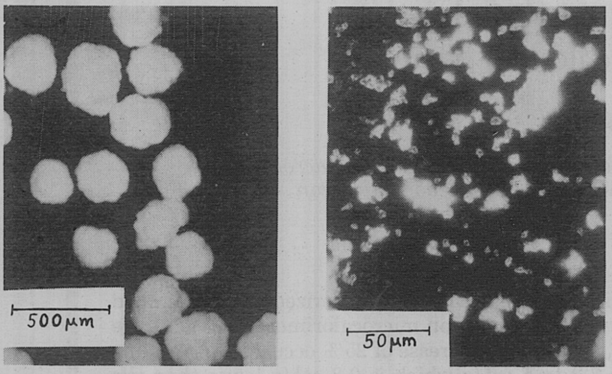


(i) as-received resin (ii) ball-milled resin

Figure 1. Optical micrographs of the PVC particles.

Table I
Enthalpies of Ball-Milled and Annealed PVC Samples at 37 °C (Calorie per Gram of Polymer)

	as is	annealed
as received	$5.8_1 \pm 2\%$	$5.9_5 \pm 2\%$
ball milled	$7.2_0 \pm 2\%$	$5.0_8 \pm 2\%$

120-101-11) at 35 kV and 16 mA and nickel filtered. A Debye–Scherrer camera of 5.73 cm radius was used to take the diffraction patterns. The sample specimen was packed into a 0.3-mm thin-wall glass tube ($^1/_{100}$-mm wall thickness). The patterns were recorded photographically on Kodak medical "no screen" films.

2. Wide-Angle X-ray Diffractometry. An X-ray generator (type 12215/0) was used in combination with a vertical diffractometer for intermittant mode reflection diffractometry. The X-ray beam passed through a primary beam slit before it hit the sample specimen located on the axis of the diffractometer. The reflected diffraction beam was collimated with a pair of diffracted beam slits and a LiF crystal before it reached a proportional counter connected to a signal synthesizer (Norelco 2000-2070). The intensity was digitally printed out on a teletype.

C. Viscometry. A Ubbelohde viscometer (Cannon Cl. 769) was used for the viscosity measurements at 46.4 °C employing acetophenone as the solvent. Only the as-received and ball-milled samples were tested for variations in molecular weight.

D. Scanning Electron Microscopy (SEM). A JSM-U3 scanning electron microscope was operated at 15.5 kV with a magnification of 5000×. The samples in powder form were placed on cylindrical aluminum specimen mounts and gold coated for 1.5 min. These were then examined at either 0 or 45° tilt, and representative spots were selected for photography.

Results

Optical micrographs of the as-received and ball-milled samples are shown in Figure 1. The resin particles or grains are about 200 µm in diameter and appear identical both before and after annealing of the as-prepared resin.

For the ball-milled resins, the smallest particles observed range from about 0.5 to 2 µm. It was impossible to determine if the larger particles observed in the photographs are weakly bound clumps of the smaller particles or remnants of the original resin particles which were not yet broken apart (agglomerates). Scanning micrographs of some of the larger particles do indeed indicate that some are remnants of the original resin particles and have not yet been broken apart by milling.

A. Enthalpy Measurements. The enthalpies of the various samples at 37 °C are listed in Table I.

Examining the relative enthalpies for the treated samples, we can see that ball milling results in an increase in enthalpy of 1.4 cal/g (5.86 J/g) over the as-received resin. But even more significant, the annealing of the ball-milled samples reduces the enthalpy by as much as 2.12 cal/g (8.87 J/g), which is still 0.73 cal/g (3.06 J/g) below the original as-received sample. On the contrary, annealing of the as-received sample does not significantly change the enthalpy, the slight variation of less than 0.15 cal/g (0.63 J/g) being within the range of experimental error.

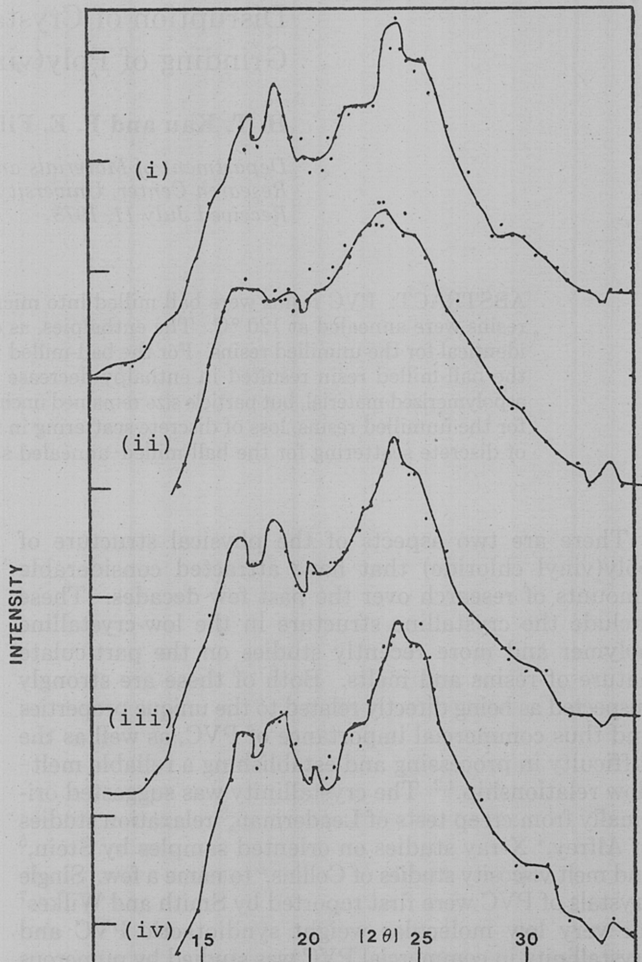
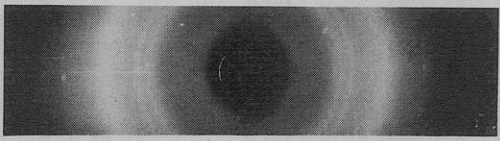
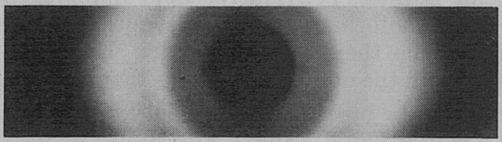


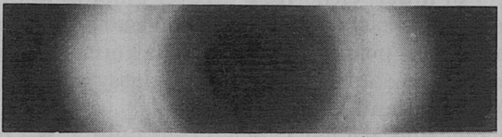
Figure 2. X-ray diffraction patterns for PVC samples: (i) as received; (ii) ball milled; (iii) as received and annealed; and (iv) ball milled and annealed.

There is a very important point which should be recalled here with regard to these measurements which is critical to later discussion. These enthalpies are measured directly and isothermally using techniques of microcalorimetry to measure heats of solution.[28] Thus solution is a requirement of this method, and for a heat of fusion of a crystalline material to be detected by this method requires that the crystallite be dissolved. This is important because it means that the crystallites we are detecting are soluble and therefore not of the syndiotactic single crystalline type morphology, i.e., either another type of morphology or more likely very imperfect crystallites.

B. X-ray Diffractometry. In Figure 2 the recorded intensity from the reflection diffractometry is plotted against the diffraction angle 2θ for each of the samples. Although quantitative analysis is handicapped by some data scattering, it is clear that the ball-milled sample gives a very different pattern, especially with respect to the discrete peaks at 2θ = 17.2 and 23.6°. These peaks correspond to spacings of 5.0 and 3.2 Å, respectively [diffraction by the (200) and (210) planes according to the analysis of PVC crystal structure[5]]. Furthermore, the peak at 2θ = 19.0°, normally of stronger intensity, is barely


(i) As-received


(ii) Ball-milled


(iii) As-received and annealed


(iv) Ball-milled and annealed

Figure 3. Debye–Scherrer powder patterns for PVC samples.

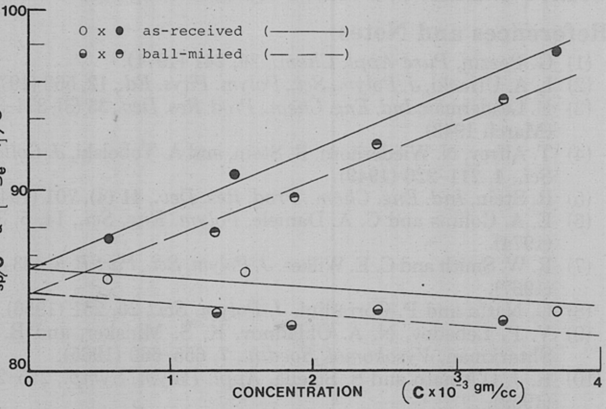
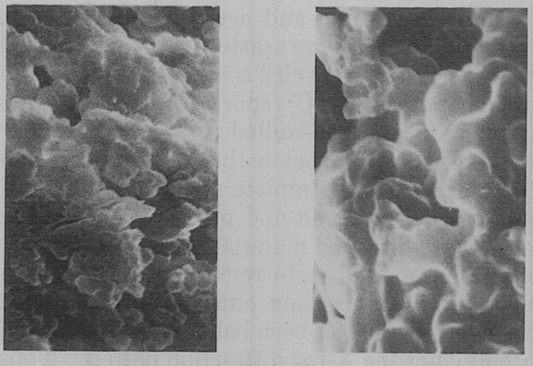


Figure 4. Plot of η_{sp}/c and ln η_r/c vs. c for PVC in acetophenone at 46.4 °C.

discernable, and a hump at about $2\theta = 30°$ is very diffuse. The Debye–Scherrer powder patterns show only two diffuse halos for the ball-milled material as shown in Figure 3, with no obvious evidence of discrete scattering. This behavior is quite different from the patterns for the other samples which show much sharper peaks in those angular positions. The annealed ball-milled sample seems to have improved discrete peaks at $2\theta = 17.2$, 19.0, 24.0, and 30.0 over the as received or its annealed sample. However, the noise-to-signal ratio is still too severe to allow a quantitative comparison. The Debye–Scherrer powder patterns from these three samples look very similar as can be seen in Figure 3, and the discrete scattering is clearly evident in the photographs.

C. Viscometry. Only the ball-milled and the as-received samples were tested to check if there was a change in the molecular weight after the mechanical treatment. The results are shown in Figure 4, where the intercepts give intrinsic viscosity of 84.2 and 85.6 cm^3/g for the ball-milled and as-received samples, respectively. Since the difference is still within the normal data scatter for such a measurement, the result indicates no significant change in the molecular weight which is related to the intrinsic viscosity for a polymer.


(i) As-received

(ii) Ball-milled

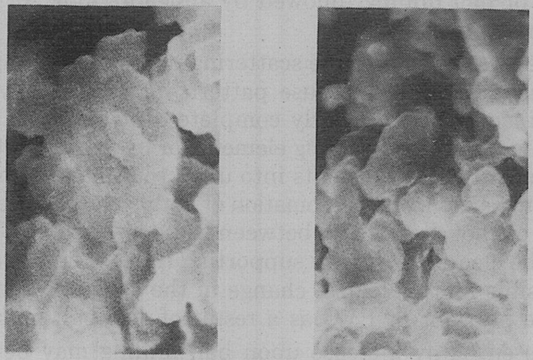

(iii) As-received and annealed
(iv) Ball-milled and annealed

Figure 5. Scanning electron micrographs of different PVC samples used in this study.

D. Scanning Electron Microscope (SEM). Scanning micrographs of small portions of the as-polymerized and the as-polymerized–annealed grains or resin particles as well as micrographs of portions of some of the larger particles (typically ~10 μm in diameter) remaining in the ball-milled samples are shown in Figure 5. The smallest particles that can be discerned in the pictures are those of about 1 μm, corresponding to the primary particles for suspension polymerized PVC. The size of the particles is nearly the same for all samples. Actually, in direct observation the apparent size of the primary particles in the ball-milled sample seems to be slightly larger, i.e., 3 to 4% larger than the as-received sample. This is of course not expected, but again the difference is not significant because an error of 5% is not uncommon in the SEM magnification.

The photographs of the ball-milled samples also seem to indicate that these agglomerates[25] are incompletely ground portions of the original grains or resin particles as opposed to loosely bound clumps of smaller particles formed, for instance, by electrostatic attraction of the small particles. However, these photographs may be misleading due to the conductive gold coating over the samples.

Discussion

To summarize, during the process of ball milling a PVC resin under very mild conditions, the resin particle sizes which were initially around 200 μm in diameter were reduced to particles which were, for the most part, in the size range of primary particles. Coincidental with this process are observed a substantial enthalpy increase of

25% within the sample and a virtual complete disappearance of discrete X-ray scattering present in the material before ball milling, which is identical to that for other radical polymerized PVC reported in the literature.[11] Upon annealing the ball-milled resin, the enthalpy decreased to a value 15% below that of the initially as-received material, while complete recovery of the discrete X-ray scattering occurred and possibly to an enhanced level over the as-received material. However, the particle size of the ball-milled resin remained unchanged upon annealing. On the other hand, annealing of the as-received material which had never been ball milled affected neither the enthalpy nor the X-ray diffraction pattern. Thus the changes observed are clearly a consequence of ball milling alone or ball milling followed by annealing but not annealing alone.

The loss of the discrete scattering upon ball milling to produce a standard diffuse pattern for PVC[11] may be explained either by nearly complete destruction of the order within the diffracting elements or by fragmentation of the diffracting elements into units too small to give a discrete pattern, or a combination of both. The X-ray data alone cannot distinguish between these alternatives, but it is the clearest evidence supporting the occurrence of a reversible morphological change in the ordered or crystalline portions of PVC as a result of this ball milling.

The enthalpy increase upon ball milling may be explained as being due to increased macroscopic inhomogeneities incorporated upon ball milling, nonfavored high-energy conformations forced into the chain upon ball milling, disruption of ordered or crystalline regions, or a combination of all three. Unfortunately, no experiment (except maybe X-ray diffraction in some cases) exists which can separate or distinguish between these three. Krimm et al.[30] have shown by infrared studies that nonfavored conformations are introduced into urea–PVC complexes upon pressing the samples. He further relates this to a reduction in crystallinity within the samples. In similar studies performed by us on atactic polystyrene and poly(methyl methacrylate),[31] no change in X-ray diffraction patterns was observed in either sample upon ball milling or subsequent annealing. For polystyrene also no change whatever was observed in enthalpy. However, for PMMA, an enthalpy decrease was observed upon ball milling the quenched sample. This behavior is related to a transition at 55 °C and discussed elsewhere.[32]

In another study[33] involving quenching and slow-cooling samples of PVC from various temperatures between 37 and 220 °C, negligible differences were observed in enthalpy for samples quenched and slow cooled from below about 130 °C, which is 45 °C above its T_g. Likewise, the enthalpy difference between the samples quenched and slow cooled from above 190 °C was essentially constant and equal to 1.4 cal/g which is nearly equal to the difference observed between our as-received and ball-milled samples. The behavior in this study was related to the fusion of the crystalline portions of the PVC samples used. Both macroscopic inhomogeneities and conformational differences certainly occur between the quenched and slow-cooled samples, but these account for at most only a few percent difference in the enthalpy between the samples. Thus, although the enthalpy increase observed upon ball milling this PVC sample can have many explanations, we feel that there is reasonable evidence to support the suggestion that it certainly could be due to disruption of crystalline or ordered regions. Further, the enthalpy data is supportive of the X-ray observations.

The decrease or recovery of the enthalpy of the ball-milled sample upon annealing is consistent with the recovery of the discrete X-ray scattering upon annealing and suggests that the morphological changes induced into the PVC by the ball milling or mechanical grinding are reversible by appropriate thermal treatment. Unfortunately, all three proposed explanations for the enthalpy increase upon ball milling, i.e., macroscopic inhomogeneities, high-energy conformations, and disruption of order are expected to be thermally reversible. However, to be consistent with the other observations that no changes are observed in the enthalpy or X-ray diffraction pattern of the as-received material upon annealing, the most reasonable explanation for the enthalpy to anneal to a value lower by 15% than the as-received material is related to recovery of order, either to a greater amount and/or increased perfection over the original morphology. That such a phenomena is possible is supported by numerous studies on strain-induced crystallization of glassy poly(ethylene terephthalate) and other polymers.[34,35]

In conclusion, we have shown that mildly ball milling a PVC resin can destroy those morphological elements which give rise to discrete X-ray scattering in PVC. Subsequent annealing of the ground material above T_g results in a reformation of the diffracting elements to a greater quantity and/or perfection than in the original material. These observations are supported by direct enthalpy measurements obtained from solution microcalorimetry measurements.

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

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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

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