

Cryogenic Crushing of Polystyrene

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Synopsis

Atactic and isotactic polystyrene powders were fractured with a ball mill at -196°C . The molecular weight distributions at various milling times measured by GPC show an initial asymmetric broadening and then a gradual returning to the original narrow bell-shaped distribution. Analysis of molecular weight distributions suggests a preferential chain scission near the chain ends. X-ray diffraction spectra of isotactic polystyrene samples show that after 24 hr of milling, the semicrystalline polystyrene was completely transformed into an amorphous polymer. DSC thermogram of the milled isotactic polystyrene reveals several crystallization peaks preceding melting when the samples were heated.

INTRODUCTION

The degradation of polymers by heat,^{1,2} γ -ray radiation,³ and ultrasonic,⁴⁻⁶ chemical,⁶ and mechanical action^{7,8} is a subject which has been studied widely. Mechanical degradation can be caused by shear,⁷ extrusion,⁸ milling,⁹ etc.

The characteristics of chain scission which occur in polymer degradation are dependent on the mode of degradation. Thermal^{1,10} and chemical⁶ degradation causes chain scission to occur randomly along the length of the chain. Ultrasonic degradation favors the scission of the chain near the central part.⁴⁻⁶ The chain scission in the extrusion of polystyrene melt⁸ suggests that thermal degradation is activated by the mechanical energy provided by the shearing action. The degradation of polyisobutene solution⁷ in laminar flow is predominantly a random process.

In the case of solid semicrystalline polymers, mechanical action produces not only chain scissions but also transformation of the crystalline structure which remains stable over a wide temperature range; for example, rolling,¹¹ drawing,^{12,13} and milling⁹ of polyethylene causes an orthorhombic-monoclinic transformation.

In this research, we try to clarify the fundamental aspect of the degradation of polystyrene, both atactic and isotactic forms, induced by ball milling at -196°C . We then investigate how the milling affects the physicochemical properties of the polymer.

EXPERIMENTAL

Material. The polystyrene samples used are standard atactic polystyrene, \bar{M}_n of 2.00×10^6 and $\bar{M}_w/\bar{M}_n < 1.30$, supplied by Pressure Chemical Co., Ltd.; and isotactic polystyrene supplied by Toray Industries Inc.

Milling Procedure. The polystyrene samples in powder form were milled at -196°C in the presence of air in a glass cylindrical vessel with a diameter of

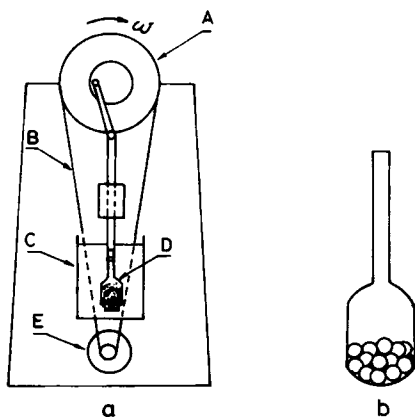


Fig. 1. (a) Schematic diagram of the ball mill apparatus. A, pulley; B, belt; C, metal Dewar flask containing liquid nitrogen; D, glass vessel with glass balls where the polymer powder was crushed; E, driving motor. (b) Enlarged diagram of D.

4 cm and a height of 5 cm. The vessel contained 25 0.9-cm-diam glass balls [Fig. 1(b)]; it was vibrated at a rate of 130 cycle/sec with a stroke 4 cm long [Fig. 1(a)]. The polymer powder was crushed by the impact of the glass balls. Crushed sample was withdrawn stepwise from the vessel after a certain milling time. The sample was milled at -196°C to prevent the thermal effect on the degradation of the polystyrene sample.

GPC Measurement. Molecular weight distribution of atactic polystyrene was measured with GPC HLC 802R manufactured by Toyosoda Co., Ltd., at room temperature, using a GMH6X2 column with 7.4 mm i.d. and 120 cm length. The samples were dissolved in tetrahydrofuran (THF). The concentrations were adjusted to about 0.16 wt %. The mobile phase was THF, and the flow rate was 1.4 ml/min. The molecular weight–elution volume calibration curve was obtained from standard polystyrene samples of Toyosoda Co., Ltd. The average molecular weights were calculated from the molecular weight distribution curve by an on-line computer CP-8 model III.

X-Ray Diffraction. X-Ray diffraction spectra of isotactic polystyrene were measured with wide angle x-ray diffractometer D-3F manufactured by Rigaku Co., with a $\text{CuK}\alpha$ tube and Ni filter.

DSC Thermogram. DSC thermograms were obtained from a standard-type DSC manufacturer by Rigaku Co., using a heating rate of $10^{\circ}\text{C}/\text{min}$.

RESULTS AND DISCUSSION

GPC Measurement of Atactic Polystyrene

GPC measurement was performed on atactic polystyrene to study the manner in which molecular weight and molecular weight distribution vary with milling time. The molecular weight distribution curves obtained at various milling times are shown in Figure 2. The starting polystyrene sample is a monodisperse polymer with narrow peak centers at about 2.00×10^6 . In the early stage of milling, the main peak moves a little to the lower-molecular-weight side, and a pronounced increase in shorter chain population at the lower-molecular-weight

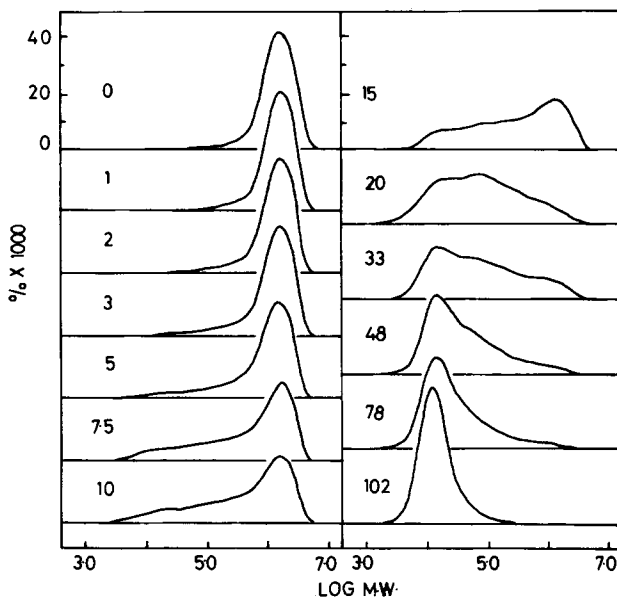


Fig. 2. Molecular weight distributions of atactic polystyrene at various milling times. Numbers at left-hand side indicate number of milling hours.

tail is observed. After about 10 hr of milling, a minor peak starts to appear at about 4×10^4 , at 20 hr of milling time; the molecular weight distribution curve appears to be composed of three components with the peak position centers at 9×10^5 , 1×10^5 , and 1×10^4 , respectively. Further milling causes the two peaks at the higher-molecular-weight side to flatten and the overall molecular weight distribution to become narrower. Finally, at about 102 hr of milling time, the molecular weight distribution regains the original bell shape and becomes relatively sharp, with peak centers at 1×10^4 .

From the results of GPC measurement, it is worthwhile to comment on the position of the scission bond of the main chain.

For a random main chain scission process, Kotliar^{14,15} as well as David³ using statistical theory predicted a change in the value of $\overline{M}_w/\overline{M}_n$ that tends toward 2. That is, for an initially broad molecular weight distribution polymer, there will be a narrowing of molecular weight distribution, and for an initially narrow molecular weight distribution, there will be a broadening of molecular weight distribution, with the asymptotic value of $\overline{M}_w/\overline{M}_n$ equal to 2. This prediction was well supported by experimental results.^{7,8} Our result in Figure 3 shows an initially rapid increase and a later gradual decrease in $\overline{M}_w/\overline{M}_n$, but at no time does the value of $\overline{M}_w/\overline{M}_n$ approach 2. Furthermore, the appearance of the molecular weight distribution at intermediate stages of milling also suggests that the broken chains are composed of two or more components of molecular weight distributions. Therefore, it is quite evident that the chain scission in our case does not occur randomly along the chain length but rather occurs as a preferential process.

In the case of preferential scission of the main chain, the preferred broken bond could be either near the center or at the chain end. The study of ultrasonic degradation of polymers established that the main chains of the polymers were

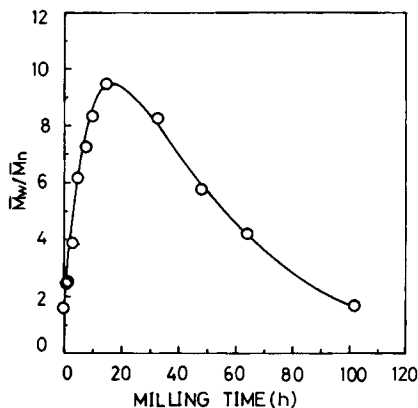


Fig. 3. Change in $\overline{M}_w/\overline{M}_n$ with milling time.

preferably broken at the C—C bonds near the center part.⁴⁻⁶ Figure 4 shows the \overline{M}_n and \overline{M}_w -versus-time plot for our result and that of ultrasonic degradation⁶ (inset in Fig. 4). The latter shows an initially rapid decrease in both \overline{M}_n and \overline{M}_w and a leveling off at the later stage, the decrease in \overline{M}_n and \overline{M}_w being parallel at approximately the same rate. Our result shows an initially rapid decrease in \overline{M}_n but a relatively slower decrease in \overline{M}_w . This could be interpreted as initially, the scissions of the chains occur near the chain ends to produce numerous short chains which lower \overline{M}_n rapidly but contribute very little to \overline{M}_w . Simha,¹⁶ in a theoretical study of the chain scission process, derived an $\overline{M}_w/\overline{M}_n$ -versus-degrading time relation for a near-chain-end scission process which is quite similar to our result. In addition, the minor peak which appears near the lower molecular weight distribution tail at the intermediate stage of milling also points to a bias in favor of the production of short chains, hence a preferential near-chain-end scission process.

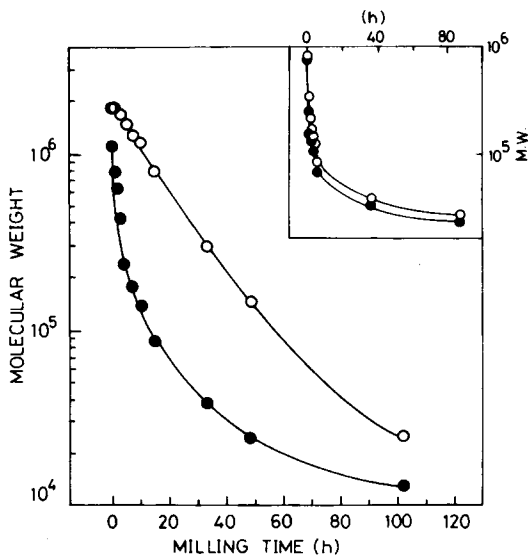


Fig. 4. Change in \overline{M}_w and \overline{M}_n of atactic polystyrene with milling time. Figure in inset at top right-hand corner is the result of ultrasonic degradation of Smith⁶: (O) \overline{M}_w ; (●) \overline{M}_n .

A reason for the preferred bond scission near the chain end can be found if we recall that, in the solid state, fracture of the polymer powder by the action of milling occurs mainly near the powder surface; as a result, chain scissions probably occur mainly on the short section of chains located near the powder surface.

X-Ray Diffraction

In order to investigate how milling affects the crystal structure of crystalline polystyrene, x-ray diffraction spectra of isotactic polystyrene powder were taken (Fig. 5). The spectrum of the original sample [Fig. 5(a)] corresponds to a rhombohedral crystal structure of isotactic polystyrene. As milling time progresses, the intensity of the reflection from the rhombohedral structure decreases; and finally, after about 24 hr of milling [Fig. 5(d)], the spectrum becomes a single broad peak identical to the halo of an amorphous polymer. The original rhombohedral spectrum is completely recovered when the 24-hr milled sample is annealed at 175°C for about 2 hr [Fig. 5(f)]. However, annealing at 105°C for 9 hr only partly restores the original crystalline structure [Fig. 5(e)].

It is well known that when crystalline polymers are subjected to mechanical action such as rolling, drawing, and impact, etc., phase transformation occurs because of slipping and twinning of the molecules in the crystalline region.^{10-13,17,18} To our knowledge, however, complete transformation from the crystalline to the amorphous phase has never been reported before. When

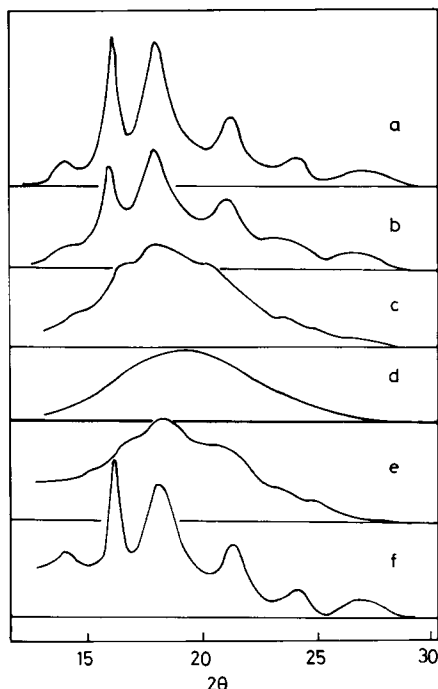


Fig. 5. (a)–(d) Changes in x-ray diffraction spectra of isotactic polystyrene with milling time for 0, 1, 5, and 24 hr, respectively. (e), (f) Effect of annealing on the recovering of crystalline structure at 105°C for 9 hr and 175°C for 2 hr, respectively.

high-density polyethylene was subjected to the same procedure of milling in our laboratory, an orthorhombic to monoclinic phase transformation occurs; but after a certain milling time, the amount of deformed crystal becomes saturated, and further milling up to 100 hr produces no change in the x-ray spectra.¹⁹

DSC Measurement

To find out how the changes in molecular weight and crystal structure affects the melting point of the sample, DSC measurement was carried out. The DSC thermograms of the samples at various milling times are shown in Figure 6. The original isotactic polystyrene sample shows a melting peak at about 222°C [Fig. 6(a)]. Milling does not affect the melting temperature. Prior to melting, however, several exothermic peaks are observed. These peaks seem to correspond to the recrystallization of the milled sample from the amorphous phase. The number of the recrystallization peaks increases with milling time. Their positions also vary with milling time. The peak at about 150°C is the first one observed, followed by those at about 86 and 110°C, respectively. These results indicate that crystallization from the deformed polystyrene sample occurs stepwise at several temperature ranges. Unfortunately, our data are not sufficient for the exact determination of the source of each crystallization peak. In Figure 6, the DSC thermograms of the annealed samples show that 9 hr of an-

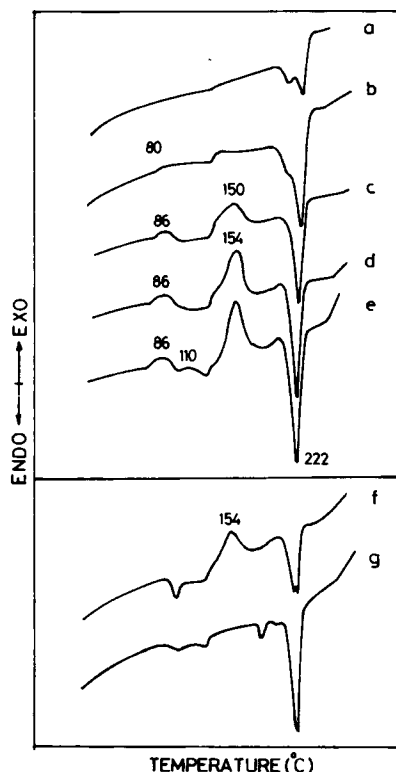


Fig. 6. (a)–(e) DSC thermograms of isotactic polystyrene showing effect of milling on the melting point for 0, 1, 5, 12, and 24 hr of milling, respectively. (f), (g) Effect of annealing at 105°C for 9 hr and 175°C for 2 hr, respectively. Numbers indicate positions of the peaks in °C.

nealing at 105°C [Fig. 6(f)] does not affect the exothermic peak at 154°C but causes those at 86 and 110°C to disappear. Annealing at 175°C for 2 hr [Fig. 6(g)] eliminates all the crystallization peaks. These results further confirm that the crystalline structure can be recovered completely only when it is annealed at a temperature close to the melting point.

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