CHEMISTRY LETTERS, pp. 1503-1506, 1987.

Decrease of Molecular Weight of Polystyrene by Ball-milling

Kimitoshi FUKUNAGA* and Makoto KIMURA
Faculty of Engineering, Yamaguchi University, Tokiwadai, Ube 755

Mechanochemical degradation of monodispersed polystyrene by a ball mill has been studied. A consistent bimodal mode of the degradation was observed for all monodispersed polystyrenes examined. From this mode of the degradation, information on the distribution of a degraded polymer molecule was obtained.

The mechanochemical degradation of vinylpolymers has emerged as a fundamental problem of major industrial importance, and the effects are important in the processing and the practical properties of polymers.[1)] Most of the experimental work with a ball mill, however, has been based only on the average molecular weight change as a result of degradation, and a detailed discussion of the degradation behavior has not been published. We report hereon the mechanochemical degradation of polystyrene (PS) which has narrow molecular weight distribution (MWD) by ball-milling. Interpretation of the degradation behavior was simplified by the use of gel permeation chromatography (GPC) to determine the changes in MWD.

Three narrow distribution PS standards were used, having weight-average molecular weights (M_ws) of 4.48×10^4 (PS-1), 1.93×10^5 (PS-2), and 8.22×10^5 (PS-3). A commercial PS of a broad MWD, $M_w=2.06\times10^5$ (PS-4), made flakes as monodispersed PSs by reprecipitation (benzene-methanol), was also used. Degradation experiments were carried out with a small ball mill (net volume:0.24 l) with two sizes of ceramic balls (15.5 and 10.3 mm in diameter), in which 2.1 g of PS was charged, at a constant velocity of revolution (205 rpm) and a packing ratio (26.3%) at room temperature. The changes in number-average molecular weight (M_n), M_w, and MWD caused by mechanochemical degradation were evaluated by GPC. A Toyo-Soda GPC Model 802UR equipped with two mixed gel columns and RI detector was used. The instrument conditions were: elution solvent, THF; temperature, 40 °C; flow rate, 1 ml/min. Size reduction of PS particle was measured by means of a scanning electron microscope (Fig.1), and the parallel decreases in M_n and particle size of PS with the progress of a milling were confirmed.

Figure 2 shows the changes in MWD of PSs by ball-milling. Peak counts (C_i) given in Fig.2 are used as a precise molecular weight (M_i) scale in terms of the relationship ($\log M_i=12.491-0.273C_i$) under the analytical conditions. GPC results for PS-2 and PS-3 before completion of degradation reveal clearly the bimodal nature of the distributions: peaks at higher and lower molecular weight in each case clearly represents portions of the original unchanged and the degraded PS

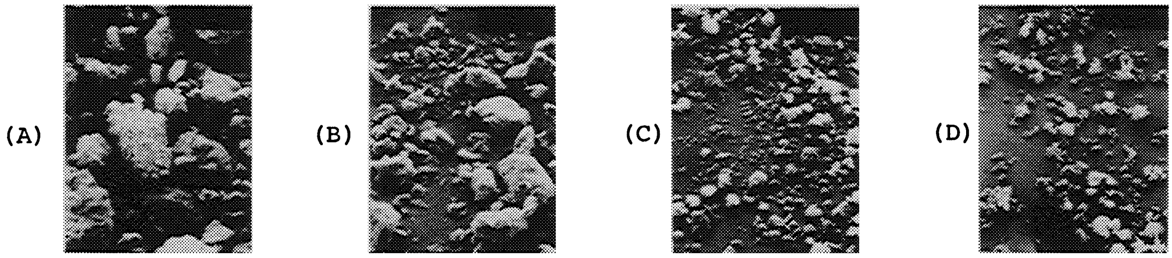

Fig.1. Scanning electron micrographs of typical PS particle (degraded PS-3). (A) 50 h (B) 100 h (C) 200 h (D) 400 h (magnification ×1000)

respectively. In the case of PS-1, elution patterns of GPC were obtained as an overlapping curve and hence resolved into two components by means of the curve analysis.[2] This is demonstrated in Fig.3. Thus, the degradation mode of PS-1 is also similar to that of PS-2 or PS-3.

The present degradation behavior is of much interest, because in general the narrow distribution of the original PS is broadened accompanying a prodominant change in the peak position by randam degradation due to shear.[3] The changes in heterogeneity index, $H=M_w/M_n$, are almost identical for all PSs including poly-dispersed PS-4: the index H increases rapidly in the beginning and then after about 200 h decreases gradually to 1.2 - 1.7. Such changes in H[4] also supports that the present degradation proceeds via nonrandam chain-scission mechanism.

There have been several previous works based on selective chain-scission. For ultrasonic degradation of PS of narrow MWD clearly showed a preferential breaking near the center of molecule.[5] Apart from the degradation of PS, a bimodal distribution due to shear degradation of poly-isobutene solutions has been reported.[6] In this case, however, both peak positions of the original and generated polymers in MWD shift with experimental conditions, and it was concluded that the bimodal distribution results from the shear degradation through chain segments

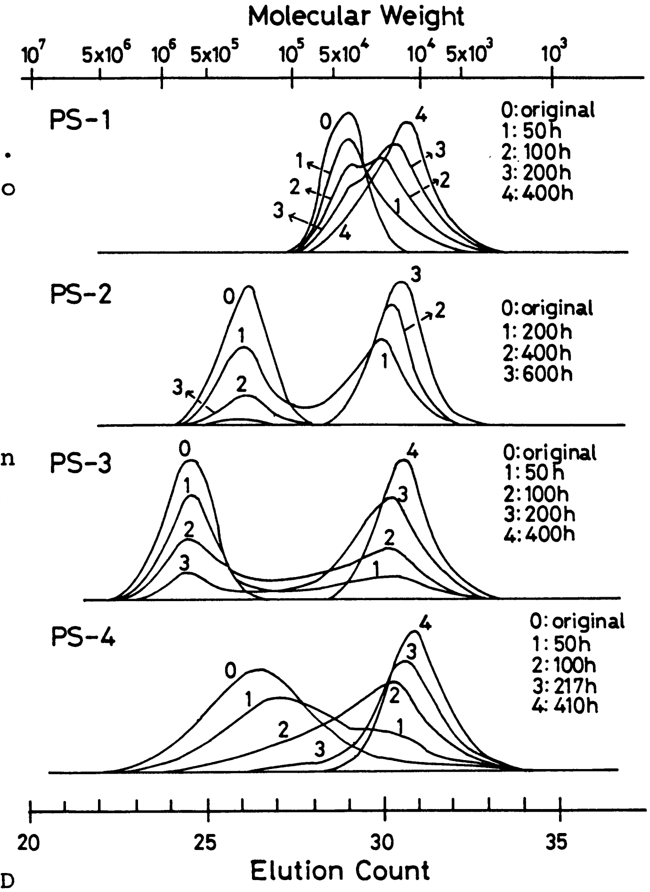

Fig.2. MWDs of PSs at various stages of degradation. Changes in M_w and heterogeneity index H were as follows:

PS-1; 0(45000;1.04) 1(35000;1.31)
2(29000;1.39) 3(23000;1.51)
4(17000;1.55)
PS-2; 0(193000;1.13) 1(86000;2.75)
2(40000;2.15) 3(18000;1.18)
PS-3; 0(822000;1.17) 1(675000;8.25)
2(267000;9.10) 3(50000;3.28)
PS-4; 0(68000;3.03) 1(37000;4.02)
2(20000;3.60) 3(12000;3.54)
4(9000;1.68)

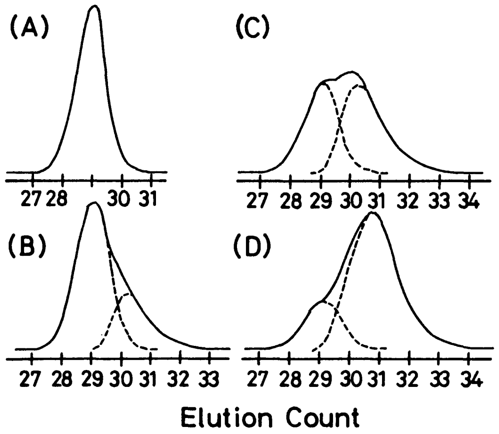

Fig.3. The resolution of gel permeation chromatogram for PS-1 series (A)original (B)50 h (C)100 h (D)400 h

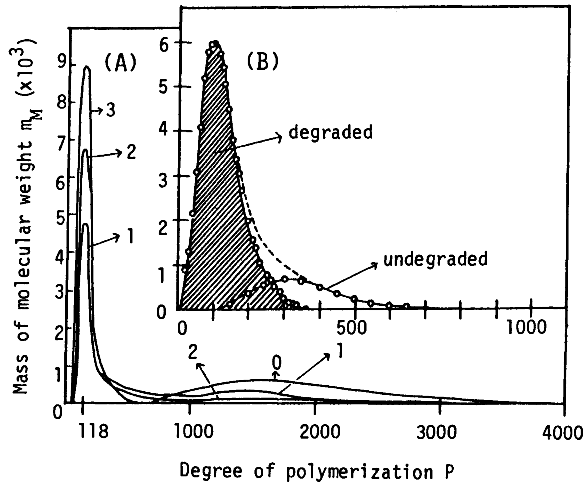

Fig.4. Mass distribution (m_M) curves.
(A)PS-2:0(original);1(200 h); 2(400 h);3(600 h)
(B)PS-1(400 h)(obtained from the resoluted curve(D) in Fig.3)

(entanglement) rather than individual chain deformations.[6] The present results differ from those distinctly. It has been considered that when mechanical shear force is applied to PS in the solid state, only the surface layer of PS undergoes a strong shearing even under high pressure by comparison of the average life times of growing polymer radical in sheared PS in solution and in solid.[7] It therefore seems most likely that the present mechanochemical reaction occurs first at the outer skin of PS particle, the zone of the reaction then moves into the solids, and may leave behind completely degraded PS and undegraded core of PS which shrinks in size during the mechanochemical reaction (surface-layer degradation).

Figure 4 shows mass distribution (m_M) curves, obtained from elution patterns, on the degradation results for PS-2 and PS-1 (400 h). From m_M data on all PSs examined it was found that there is essentially no variation in the peak position of polymers produced by degradation. Thus, the limiting degree of polymerization (P_l), below which polymer will not degrade further, of PS in milling is 118. This value is considerably lower than the 380 - 694[8] and is comparable with 125 - 130[9] reported for PS in ball-milling and in vibration ball-milling respectively.

From m_M data of the degraded polymer, it was found that distribution function of degraded polymer D(P), which means the mass fraction of polymer of the degree of polymerization P distributed from total mass of degraded PS, is represented well by the logarithmic normal distribution function (1), where b,P_0=constant.

$$D(P) = \frac{1}{\sqrt{\pi}\,\beta P} \exp\left[-\frac{1}{\beta^2}(\ln P/P_0)^2\right] \qquad (1)$$

Several workers[10,11] assumed that the rate of mechanochemical breakdown in a atmosphere of air is a linear function of the term ($P-P_l$). The effect of initial P of PS on the breakdown rate was evaluated on the basis of degree of degradation (the ratio of total m_M of the degraded PSs to the sum of total m_M of the degraded

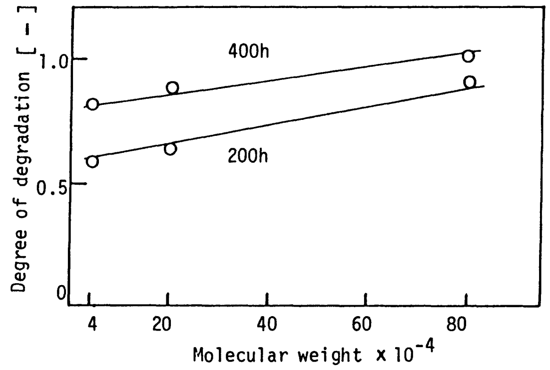

Fig.5. The effect of initial chain length on the degree of degradation.

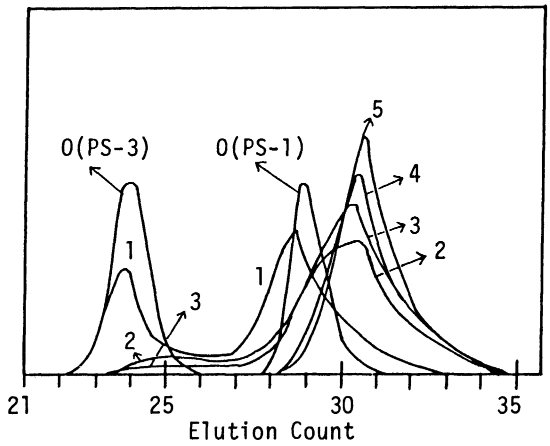

Fig.6. MWDs of the mixture of PS-1 and PS-3 at various stages of degradation.
0(original) 1(50 h) 2(100 h)
3(200 h) 4(400 h) 5(500 h, 600 h)

and undegraded PSs) in a unit time (Fig.5). When two equivalent weight of monodispersed PSs (PS-1 and PS-3) were mixed PS-3 (P=7910) disappeared more rapidly than PS-1 (P=430) as shown in Fig.6. These results also support their theory. Furthermore, the degradation rate of polydispersed PS-4, evaluated by fitting the rate equation to experimental measurement on M_n, was represented by the first order equation, $-dP/dt=0.0103(P-118)$. Consequently, the function S(P), which represents the probability a PS molecule of P to be cut off in a unit time, may be represented by Eq.2, where k=constant.

$$S(P) = k(P-P_l) \qquad (2)$$

It is considered to be probable that polydispersed PS is also broken by the same mode of degradation as that of monodispersed PS, because the change in MWD of PS-4 by ball-milling is able to well approximated by the use of Eqs. 1 and 2 assuming proper numerical values as parameters.

References

1) A. Casale, Rubber Chem. Technol., 44, 534 (1971).
2) D. Ohmori and T. Okuyama, Nippon Kagaku Kaishi, 1973, 1915.
3) K. Abbas and R. S. Porter, J. Polym. Sci., Polym. Chem. Ed., 14, 553 (1976).
4) K. W. Scott, J. Polm. Sci., Polym. Symp. Ed., 46, 321 (1974).
5) W. B. Smith and H. W. Temple, J. Phys. Chem., 72, 4613 (1968).
6) R. S. Porter, J. R. Manfred, J. R. Cantow, and J. F. Johnson, J. Polym. Sci., Part C, 16, 1 (1967).
7) Y. Ogo, Y. Okuri, and Y. Nakai, Zairyo, 30, 893 (1981).
8) Y. Kaneko and K. Sugiyama, Zairyo, 25, 679 (1976).
9) Y. Kaneko and K. Sugiyama, Zairyo, 26, 214 (1977).
10) G. Schmid, Physik. Z., 41, 326 (1940).
11) N. Kaneniwa and A. Ikekawa, Zairyo, 21, 516 (1972).

(Received April 28, 1987)