Mechanical Scission of Poly(α -methylstyrene) in Solution. The Influences of Polymer Concentration

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ABSTRACT: Poly(α -methylstyrene) ($\overline{M}_v = 4.4 \times 10^6$) was degraded by the capillary flow method in toluene at several concentrations. Molecular weight distributions of degraded polymers were determined using GPC (gel-permeation chromatography) and the reshaping method presented by Pierce and Armonas.¹ Subsequently the number of polymer molecules in each fraction was determined as a function of the reaction time t , by these distribution curves. Finally, under the assumption of a first-order reaction, the scission reaction velocity constant K_i^j was calculated using thus determined number of polymer molecules at t , where K_i^j is scission velocity constant to form i -th group from j -th group of polymers. As results, the K_i^j value increases with decreasing concentration of polymer. And in general cases, K_i^j is largest when i is equal to $j/2$. The above results mean that the scission reaction by this capillary flow method is not a simple random one, and the deviation from random scission becomes greater as solution becomes more dilute.

KEY WORDS Scission / Capillary / Poly(α -methylstyrene) / GPC /
Velocity Constant / Concentration / Degree of Polymerization /
Location of Main Chain /

The influences of polymer concentration on mechanical scission in solution have been reported by many authors. For example, Berlin² has pointed out that the kinetic expression for the ultrasonic degradation varied with polymer concentration. Goto and Fujiwara^{3,4} have proposed an expression considering the entanglement effects caused by long-chain polymer molecules, and have proved the applicability of this expression in many cases.

In this study, we assumed that the first-order kinetic expression is conserved for mechanical scission of polymers effected by the capillary flow method, and have tried to calculate each velocity constant, as a function of the location of main chains in polymer molecules, degree of polymerization, and polymer concentrations.

The assumption that first-order expression is conserved does not contradict the meaning of the expression presented by Goto and

Fujiwara,^{3,4} because K_i^j calculated in this study is considered as a constant that varies with circumstances in which each main chain is placed (polymer concentration, location in a polymer molecule, molecular weight of polymer in which they belong, etc.), whereas Goto and Fujiwara^{3,4} conserved the scission velocity constant as an invariable value. Thus there exists a difference between the two expressions.

We suppose that the first-order kinetic expression is suitable in making clear the influences of each factor and in considering the mechanism of the scission reaction.

EXPERIMENTAL

Preparation of Poly(α -methylstyrene)

Poly(α -methylstyrene) used in scission reactions was obtained by anionic polymerization, catalyzed by n -butyllithium, *in vacuo*, using THF(tetrahydrofuran) as solvent at -78°C .

After polymerization (reaction time, 24 hr) living polymer was deactivated by small amount

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of methanol, precipitated in methanol, filtered, and dried *in vacuo* at 60°C.

The molecular weight of the polymer was determined by the viscometric measurement in toluene, at 25°C, by the following relation.⁵

$$[\eta] = 7.81 \times 10^{-5} \bar{M}_v^{0.73} \quad (1)$$

Scission Reactions

The apparatus shown in Figure 1 was used for the scission reaction. The capillary part is fabricated from stainless-steel, and other parts are from brass.

Figure 1. Apparatus for the scission of polymer molecule in solution: A, N₂ gas inlet; B, sample inlet; C, Kel-F O-ring.

Polymer solutions in toluene are poured into the apparatus from the sample inlet through a glass filter. After packing this inlet with a screw and Kel-F O-ring, pressure is adjusted with nitrogen from a tank *via* a pressure regulator. This operation cycle is repeated for the desired number of times.

After the desired operation cycles, sample portions are removed and concentrated by evaporation at room temperature *in vacuo*, then

poured into methanol to precipitate polymers. Polymer samples are filtered and dried *in vacuo* at 60°C. The remainder of the polymer solution after sample removal is used for continuing the scission reaction.

Reaction times are determined by the following relation from observed value T .

$$t = \left[\frac{L \cdot S \cdot T}{V} \right] n \quad (2)$$

where, t , L , T , S , and n are the reaction time, capillary length, time for the flow out of the solution of volume V , cross sectional area of capillary, and the number of flow out, respectively.

Gel-Permeation Chromatography

Measurement. Polymer samples are dissolved to form 0.3-g/dl THF solutions, and filtered with asbestos filter. These solutions are analyzed by a Water Instrument, equipped with sets of columns packed with polystyrene gel. The conditions for measurements are as follows.

3 columns for sample solution;
porosity, 10⁷, 10⁶, and 10⁵ Å

3 columns for reference;
porosity, 10⁴, 10³, and 10² Å

Reshaping of GPC. Reshaping of GPC was carried out with the method presented by Pierce and Armonas,¹ applying the following

Figure 2. Observed (—●—) and calibrated (—○—) GPC for raw polymer.

equation to 20 points of GPC charts

$$W(v) = \left[\frac{h}{h-c} \right]^{1/2} F(v) \exp \left[\frac{-b^2}{4(h-c)} \right] \quad (3)$$

where $F(v)$ is the observed function, h is the constant determined by GPC, using almost monodisperse poly(α -methylstyrene) samples (obtained by anionic polymerization initiated by n -butyllithium; M_v , 3.8×10^5 – 8.4×10^5) and Tang's expression, and b , c , is $-(\partial \ln F / \partial y)$, $-1/2(\partial^2 \ln F / \partial y^2)$ at $y=v$ respectively. As result, the constant h becomes 1.887. The value b and

c are determined by numerical calculation at each elution volume y using crude GPC charts.

In Figure 2, an example of the results obtained by this reshaping for raw polymer is shown.

After reshaping, abscissa of the graph is converted to molecular weight, and all distributions thus determined are normalized using a planimeter.

In Figures 3, 4, 5, and 6, the relations between molecular weight and weight fractions at different reaction times are shown.

Figure 3. The changes of molecular weight distribution with the reaction time: polymer concn, 0.299 g/100 ml; applied pressure, 18.5 kg/cm². $n=10$ corresponds to 14.1×10^{-3} sec.

Figure 4. The changes of molecular weight distribution with the reaction time: polymer concn, 0.0998 g/100 ml; applied pressure, 14.1 kg/cm². $n=10$ corresponds to 14.4×10^{-3} sec.

Figure 5. The changes of molecular weight distribution with the reaction time: polymer concn, 0.0299 g/100 ml; applied pressure, 10.2 kg/cm². $n=10$ corresponds to 16.8×10^{-3} sec.

Figure 6. The changes of molecular weight distribution with the reaction time: polymer concn, 0.00998 g/100 ml; applied pressure, 10.3 kg/cm². $n=10$ corresponds to 16.3×10^{-3} sec.

CALCULATION OF SCISSION VELOCITY CONSTANTS

In Figures 3—6, there appear differences in the changes in the distributions of the molecular weight with increasing reaction time. To clarify the cause of these differences, scission reaction velocity constants were calculated.

For the above-described purpose, the general equation of scission reaction proposed by Simha⁶ is applied.

$$\frac{dn_i}{dt} = 2 \sum_{p=j+1} k_j^p n_p - \sum_{i=1}^{j-1} k_i^j n_j \quad (4)$$

where n_j means the number of j -mer which exist in the reaction system at time t , and k_i^j means the scission velocity constant to form i -mer from j -mer.

From Figures 3—6, we can estimate the number of j -mer (n_j) as a function of reaction time t ($n_j = w_j/j \times m$; w_j , weight fraction of j -mer; m , molecular weight of α -methyl styrene). Here the region of molecular weight distribution is divided into 13 fractions, such as (1) 2.5×10^5 — 7.5×10^5 , (2) 7.5×10^5 — 12.5×10^5 , (3) 12.5×10^5 — 17.5×10^5 , (4) 17.5×10^5 — 22.5×10^5 , ... (12) 57.5×10^5 — 62.5×10^5 , (13) 62.5×10^5 — 67.5×10^5 , and we assume that the constant to cleave the j -mer to form i -mer is the same value as the constants to cleave all polymers contained in $[mj/(5 \times 10^5)] + 1$ -th fraction (group) to form $[mi/(5 \times 10^5)] + 1$ -th fraction (group) of polymers.

Then the differential equation (eq 4) becomes as follows

$$\frac{dN_j}{dt} = 2 \sum_{p=j+1}^{13} K_j^p N_p - \sum_{i=1}^{j-1} K_i^j N_j \quad (5)$$

where N_j is the number of polymer molecules contained in j -th group at time t , and relation between k_i^j and K_i^j is expressed

$$K_i^j \simeq g k_i^{jg} \quad g = (5 \times 10^5)/m. \quad (6)$$

The assumption described above is acceptable, because the constant k_i^j may be considered as a continuous function along the polymer chain when the degree of polymerization is high enough, and there is no reason why certain main chains have very particular properties to result that k_i^j raises at particular j or i . Moreover, the ability of GPC is not sufficient to

Figure 7. The variation in number of polymer molecules contained in 10 ml of solution: polymer concn, 0.299 g/100 ml. (vi) means the group 6, that is to say, the molecular weight is 27.5×10^5 — 32.5×10^5 ; number of abscissa has the same meaning as n in eq 2 and $n=10$ corresponds to 14.1×10^{-3} sec.

Figure 8. The variation in number of polymer molecules contained in 10 ml of solution: polymer concn, 0.0998 g/100 ml. $n=10$ corresponds to 14.4×10^{-3} sec.

distinguish j -mer and $j+1$ -mer. Since we can consider that eq 5 expresses sufficiently the eq 4, the calculation according to eq 4 is meaningless, even if it is possible, in this study.

Figure 9. The variation in number of polymer molecules contained in 10 ml of solution: polymer concn, 0.0299 g/100 ml. $n=10$ corresponds to 16.8×10^{-3} sec.

Figure 10. The variation in number of polymer molecules contained in 10 ml of solution: polymer concn, 0.00998 g/100 ml. $n=10$ corresponds to 16.3×10^{-3} sec.

In Figures 7, 8, 9, and 10, the changes in number of polymer molecules contained in (1)–(13) groups are shown.

There appear more clearly the differences in the variations according to reaction times compared to Figures 3, 4, 5, and 6. For example, we can observe that a steady state continues for a rather long time in the medial groups when the concentration becomes high. On the contrary, in a very dilute system, there appears no longer such a state for any groups.

The calculation of K_i^j is carried out as follows. At $t_1, t_2, t_3, \dots, t_{13}$, the values of $N_1, N_2, N_3, \dots, N_{13}$ and $dN_1/dt, dN_2/dt, \dots, dN_{13}/dt$ can be read off from Figures 7–10. So we can obtain the following series of first-order equations.

$$\left(\frac{dN_j}{dt}\right)_{t_l} = 2 \sum_{p=j+1}^{13} K_j^p(N_p)_{t_l} - \sum_{i=1}^{j-1} K_i^j(N_i)_{t_l} \quad (l=1, 2, 3, \dots, 13) \quad (7)$$

Above series of equations are easy to solve with respect to K_i^j .

RESULTS AND DISCUSSION

The values of K_i^j calculated according to above-described procedures are shown in Figures 11, 12, 13, and 14.

Figure 11. Scission velocity constants along polymer chains as a function of molecular weight: polymer concn, 0.299 g/100 ml. For an example, K_4^{10} means the scission velocity constant to form group 4 polymers ($M_w=17.5 \times 10^5$ – 22.5×10^5) from group 10 polymers ($M_w=47.5 \times 10^5$ – 52.5×10^5). I is equal to the value $N \times m \times 10^{-4}$, where N is the number of monomer units counted from the center of polymer molecules, and m is molecular weight of α -methylstyrene (118).

Figure 12. Scission velocity constants along the polymer chains as a function of molecular weight: polymer concn, 0.0998 g/100 ml.

Figure 13. Scission velocity constants along the polymer chains as a function of molecular weight: polymer concn, 0.0299 g/100 ml.

Figures 11–14 show clearly that scission reaction in this study is, more or less, one in which velocity constants increase when the location of main chains becomes near to the center of polymer molecules. This tendency increases as the concentration of polymer decreases. On the other hand, as the concentration of the polymer increases, scission reactions approach randomness. By the consequence of this dependency of K_s^j on the concentration of polymer, the changes in distribution with the reaction times differ from each other (Figures 3–6).

Moreover, the above tendency of K_s^j means the diminishing of the particularity of the location of main chains in a polymer molecule, when the concentration of polymer increases. On the other hand, Harrington and Zimm⁷

Figure 14. Scission velocity constants along the polymer chains as a function of molecular weight: polymer concn, 0.00998 g/100 ml.

concluded that polymer molecules in capillary flow degradation are elongated linearly.

From these conclusions and results, we suppose that, in a concentrated system, the entanglements of polymer molecules in a capillary influence the scission reaction, in other words, the location of main chains in entangled and elongated polymer differ from chains in a isolated polymer molecule in capillary flow. In such a case, we may expect an averaging of the scission reaction constants. This supposition is acceptable because the tendency of averaging is not so clear in case of polymers of low molecular weight even when the concentration becomes 0.0998 g/100 ml or 0.299 g/100 ml.

We may conclude that the complexity of the expression for a scission reaction occurs from the deviation from random scission to another type of scission during the course of the reaction, in a concentrated system. At first stage of the reaction, influence of large molecules predominates, that is to say, kinetic expression is the one for random scission. Subsequently as the reaction advances, the influence of small molecules appears. Such molecules are affected only very slightly by such an averaging effect.

Whereas in a very dilute system, scission velocity constants themselves vary with the

location of main chains in a polymer molecules and degree of polymerization.

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