References

(1) J. C. Sheehan and D. H. Yang, *J. Org. Chem.*, **80**, 1158 (1958).

(2) G. E. Foley, E. F. Barell, R. A. Adams and H. Lazarus, *Exp. Cell Res.*, **57**, 129(1969).

(3) K. A. Harrap and D. E. M. Speed, *Br. J. Cancer Res.*, **18**, 809(1964).

(4) K. Y. Zee-Chang and C. C. Cheng, *J. Med. Chem.*, **13**, 414 (1970).

(5) K. Y. Zee-Cheng and C. C. Cheng, *J. Med. Chem.*, **15**, 13 (1972).

(6) H. Esterbauer, A. Ertl and N. Soholz, *Tetrahedron*, **32**, 285 (1976).

(7) B. Paul and W. Korytnyk, *J. Med. Chem.*, **19**, 8, 1002 (1976).

(8) N. Runsch, *et al.*, *FEBS letters*, **30**, 286(1976).

(9) M. Esterbauer, *Carbohydrate Res.*, **43**, 779 (1975).

(10) I. H. Hall, K. H. Lee, E. C. Mar and C. O. Starness, *J. Med. Chem.*, **20**, 3, 333 (1977).

(11) J. L. Wood and V. du Vigneaud, *J. Biol. Chem.*, **130**, 109 (1939).

(12) N. W. Pirie, *Biochem. J.*, **25**, 614 (1931).

(13) C. R. Harington and T. H. Mead, *ibid.*, **29**, 1602 (1935).

(14) A. Schoberl, *Angew. Chem. A/60*, **Nr. 11/12.** 308 (Jahrg. 1948).

(15) F. E. King, J. W. Clard-Lewis, and R. Wade, *J. Chem., Soc.*,

(16) v. J. E. Brownlee, M. E. Cox, B. O. Handford, J. C. Marsden and G. T. Yong, *J. Chem. Soc.*, 3832 (1964).

(17) R. Camble, R. Puradyatha and G. T. Yang, *ibid(C)*. 1219 (1968).

(18) G. Jung, H. Fouad and G. Heusel, *Angew. Chem. internat. edit*, **14**, 12, 817 (1975).

(19) D. E. Worral "Organic Synthesis," Col. Vol. I, p. 413 John Wiley and Sons, Inc., 1958.

(20) R. G. Kallen, *J. Amer. Chem. Soc.*, **93**, 6136 (1971).

Rheological Properties of Polystyrene Degraded by Mechanical Forces

In Joon Oh and Taikyue Ree†

Department of Chemistry Korea Advanced Institute of Science and Technology, P. O. Box 150 Chongyangni, Seoul 131, Korea

(*Received June 10, 1981*)

Polystyrene was degraded by using a vibrating ball mill. The viscosities and molecular weights of the degraded products were measured, and the decrease of viscosity η with $\dot{s}$ (rate of shear) observed for the degraded products were analyzed by applying the Ree-Eyring equation for viscous flow. The variation of the parameters $x_2/\alpha_2, \beta_2$ and $x_1\beta_1/\alpha_1$ in the equation were explained by the fracture of polymer molecules by mechanical force. The electron paramagnetic resonance spectrum of the degraded sample was taken, and it was confirmed that free radicals were produced by the chain-scission of polystyrene.

Introduction

It is well known that degradation occurs when mechanical force is applied to polymers[1]. That is, lower grade polymers are formed because of chain scission by mechanical force; as a result, the molecular weight decreases and the rheological properties change[2].

In this study, after degrading solid state polystyrene by using a vibrating ball mill, the viscosity η of degraded products was measured and the flow curves of η *vs.* shear rates were determined. The experimental results where analyzed by using the Ree-Eyring generalized viscosity equation. The results showed that the chain scission occurs by the mechanical degradation as expected. We also confirmed the free radical formation during degradation by using electron paramagnetic resonance (EPR). These results are reported and discussed in this paper.

Theory

The Ree-Eyring generalized viscosity equation based on absolute reaction rate theory is given by:[3]

$$\eta = \sum_{i=1}^{n} \frac{x_i\beta_i}{\alpha_i} \frac{\sinh^{-1} \beta_i \dot{s}}{\beta_i \dot{s}} \qquad (1)$$

where η is viscosity, $\dot{s}$ is shear rate, x_i is the fraction of area occupied by flow units of the ith group, and α_i and β_i are defined, respectively, by the following equations:

$$\alpha_i = (\lambda\lambda_2\lambda_3)_i / 2kT \qquad (2)$$

and

$$\beta_i = 1/(\lambda/\lambda_1)_i 2k_i' \qquad (3)$$

In the above, α_i^{-1} is the quantity proportional to the shear modulus of the ith flow group unit, β_i is proportional to the relaxation time, k is Boltzmann constant, T is absolute temperature, k_i is the rate constant of the flow process of the ith flow group unit, λ, λ_1, λ_2 and λ_3 are molecular parameters in the viscosity equation of Eyring,[4] and the subscript i in $(\lambda\lambda_2\lambda_3)_i$ or $(\lambda/\lambda_1)_i$ represents that the quantities inside the parentheses belong to the ith flow group.

For polymer solutions, Eq. (1) is reduced to Eq. (4), the details are referred to the reference,[5]

$$\eta=\frac{x_1\beta_1}{\alpha_1}+\frac{x_2\beta_2}{\alpha_2}\frac{\sinh^{-1}\beta_2\dot{s}}{\beta_2\dot{s}} \tag{4}$$

where the subscript 1 represents the Newtonian flow group and 2, the non-Newtonian group.

Experimental

Preparation of Sample. Polystyrene produced by Hannam Chemical Co. (Seoul, Korea) was used as the test sample. Benzene (Kanto: EP) was used as a solvent, and the thin crumbly film prepared in this laboratory was dried in a vacuum oven at least for 10 hours at 25°C in order to remove the solvent completely.

Mechanical Degradation of the Sample. The equipment used for the degradation of polystyrene was similar to that of Sakaguchi[6] (see Figure 1). Polystyrene in thin crumbly film state was placed into a small ampoule A contained glass balls of 5 to 8 mm diameter, and mechanical force was applied to the sample through the up-and-down motion of glass balls by vibrating the ampoule. The frequency of vibration was controlled by changing the rpm of the pulley P (Figure 1) 500 to 800. The time for the application of the mechanical force was 5, 8, 10, 12 or 15 hours.

Viscosity Measurement. A Cannon Fenske capillary viscometer was used. The assembly line of the viscometer was shown in other reference.[7] We obtained the viscosity data depending on the shear rate by regulating the applied external pressure. The concentration of polystyrene in benzene was fixed to 1g/dl and the temperature was kept at 25°±0.2°C.

The molecular weight M of the sample was determined by the intrinsic viscosity, whose relation is given by:[8]

$$[\eta]=KM^a \tag{5}$$

where K and a are constants. The values of K and a are 9.52×10^{-3} and 0.744, respectively, for polystyrene (solvent: benzene) at 25 °C, and we used these values for determining M from Eq.(5) by making use of the observed $[\eta]$ values.

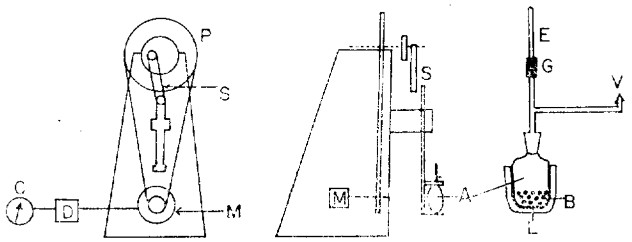


Figure 1. Schematic diagram of a vibrating ball mill apparatus and the ampoule. A, ampoule of which the enlarged portion is shown on the right; B, glass balls in ampoule A; E, EPR cell; G, graded seal; L, liquid nitrogen in a dewar flask; V, vacuum system; C, voltage control; D, bridged diod and condenser; M, motor; P, pulley; S, shaft.

Electron Paramagnetic Resonance Spectrum. Polystyrene film was placed into the ampoule A, in Figure 1, and then the system was evacuated to 10^{-5} mm Hg. The ampoule was immersed in liquid nitrogen L and then it was vibrated to crush the polymer flakes. After 3 hours of this treatment, the crushed flakes were transferred to the EPR sample tube E in Figure 1. Then the spectrum of polystyrene was taken at 77 °K by using a Varian E-4 spectrometer.

Results and Discussion

Figures 2 and 3 represent the results obtained for polystyrene degraded by the ball mill. From the figures, one notes that the viscosity of the sample decreases with the time and rpm of the mechanical operation. These facts indicate that long polystyrene molecules degrade to shorter molecules, thus the viscosity decreases. We also note that η decreases with $\dot{s}$ which is a common character of non-Newtonian liquids. The molecular weights for degraded samples were tabulated in Table 1, and one notes that the molecular weights decrease with increasing degradation time and the rpm. This fact is explained along the line of explanation

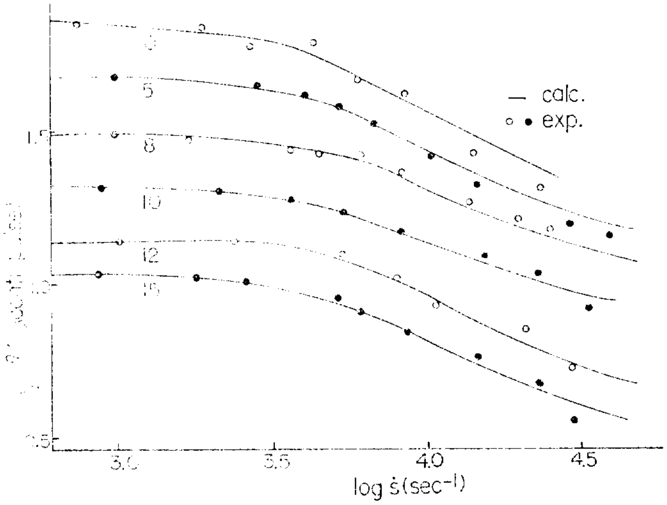


Figure 2. Viscosity η *vs.* logarithm of shear rates $\dot{s}$. Sample: polystyrene degraded for various degradation time at rpm=780 (the numbers on the curves represent the degradation time in unit of hours).

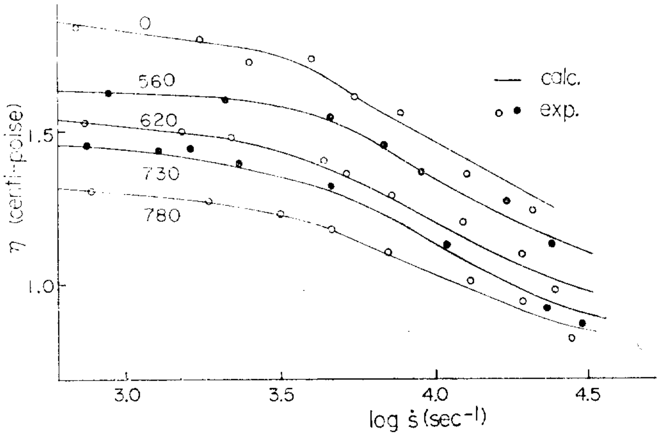


Figure 3. Viscosity η *vs.* logarithm of shear rates $\dot{s}$. Sample: polystyrene degraded for 10 hours at various rpm (the numbers on the curves represent the rpm).

TABLE 1: Flow Parameters and Molecular Weights of Polystyrene Degraded by Mechanical Force

t(hr)	rpm	$x_1\beta_1\alpha_1$ (C.P.)	x_2/α_2 (dyne/cm)	$\beta_2\times10^4$ (sec)	Mol. Wt. $\times10^5$
0	0	0.95	34.4	2.62	2.037
5	780	0.85	30.9	2.59	1.794
8		0.77	27.2	2.54	1.699
10		0.68	25.1	2.51	1.388
12		0.61	22.1	2.49	1.276
15		0.55	16.9	2.48	—
10	560	0.83	31.2	2.60	1.958
	620	0.75	30.7	2.59	1.860
	730	0.68	30.4	2.57	1.700

of the decrease in η mentioned above. By applying Eq. (4) to the experimental results shown in Figures. 2 and 3, the values of the parameters of $x_1\beta_1/\alpha_1$, x_2/α_2 and β_2 were determined, and are tabulated in Table 1. This table shows that the parameters decrease with the time and rpm. The non-Newtonian units will decrease by mechanical fracture, thus, it is expected that the parameter x_2/α_2 in Eq. (4) will decrease with the degree of degradation as one notes from Table 1. As the degradation of polymers proceeds, the chains of polymer molecules are broken, thus non-Newtonian groups become Newtonian groups, *i.e.*, $X_2\rightarrow X_1$. Though x_1 would increase with the degree of degradation, $x_1\beta_1/\alpha_1$ decreases as shown in Table 1. This is due to the fact that the increase in x_1 is overpowered by the decrease in β_1. The reason for the decrease in β_1 is as follows: the Newtonian flow units are also composed of various kinds of flow units, of which large units seem to be degraded to smaller units by mechanical force, thus β_1 turns to decrease.

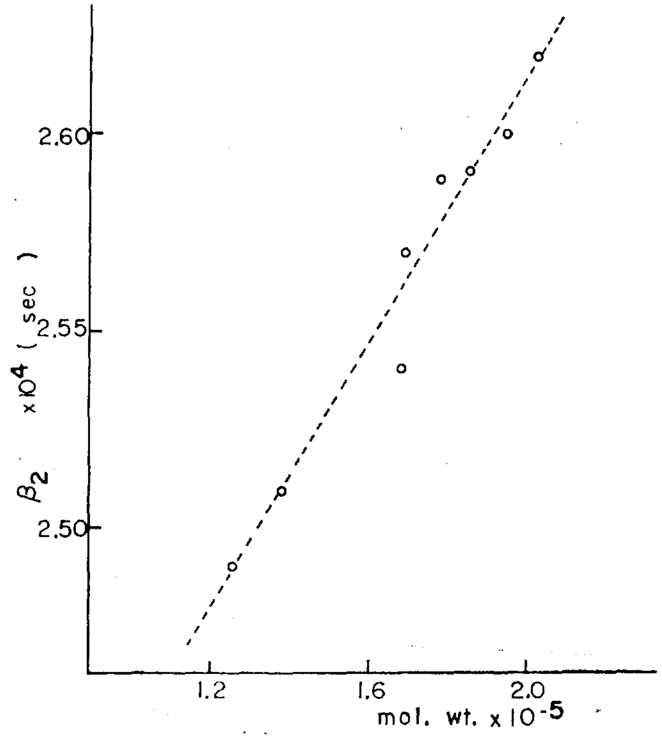


Figure 4. Relationship between "relaxation time" β and molecular weight M.

The parameter β_2 also changes with time and r.p.m. of the mechanical operation (see Table 1). This fact also shows the breaking down of non-Newtonian flow units. In Figure. 4 the parameter β_2 are plotted against the molecular weight of the degraded sample by using the data summerized in Table 1. One notes that the sample with higher molecular weight has a larger β_2. This is a natural consequence from the fact that longer molecules flow slowly. Next we consider more precisely why longer molecules flow slowly, *i. e.*, the relaxation times are large. In terms of activated complex theory β is represented by the following equations:

$$\beta=(\lambda_1/2\lambda)(h/kT)\exp(\Delta G^{\ddagger}/RT) \tag{6}$$

$$=(\lambda_1/2\lambda)(h/kT)\exp[(\Delta H^{\ddagger}-T\Delta S^{\ddagger})/RT] \tag{7}$$

$$=\beta_0\exp(-\Delta S^{\ddagger}/R) \tag{8}$$

where

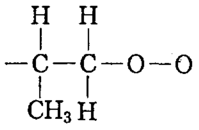
$$\beta_0=(\lambda_1/2\lambda)(h/kT)\exp(\Delta H^{\ddagger}/RT).$$

The activation enthalpy $\Delta H^{\ddagger}$ for flow will be a constant since long chain molecules execute segmental motion, and the latter requires about equal $\Delta H^{\ddagger}$ irrespective of the length of the molecules.[9] The parameter, (λ_1/λ) is considered to be about constant, thus β_0 is regarded as constant regardless of the size of the molecules. Then the difference in β with the size of molecules (or molecular weight) is due to the activation entropy $\Delta S^{\ddagger}$. It was found that $\Delta S^{\ddagger}$ for high polymers is negative.[10] This is due to the fact that in the activated complex, the molecule changes to a contracted form which is convenient for flow. Thus β becomes larger for molecules with high molecular weight in accordance with Eq. (8) since $|\Delta S^{\ddagger}|$ for longer chains is larger than for shorter chains.

We obtained the EPR spectrum shown in Figure 5. It

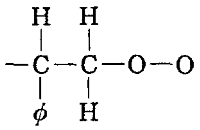
Figure 5. EPR spectrum of polystyrene degraded for 3 hours at rpm=780 (measured at 77°K).

has a similar features in comparison with the EPR spectrum obtained by other method,[11] but not the same completely. As this reason, the following is considered. In the presence of a minute quantity of oxygen, some peroxide radicals are produced by the reaction of the oxygen with radicals. In our experiment, this possibility cannot be excluded. The possibility is strengthened from the fact that the spectrum obtained from our experiment is similar to the EPR spectrum for polypropylene.[12] In the latter case, the peroxy radical (A) may be produced whereas in our case, a similar peroxy radical (B) is formed:



$-\overset{H}{\underset{CH_3}{C}}-\overset{H}{\underset{H}{C}}-O-O$

(A)



$-\overset{H}{\underset{\phi}{C}}-\overset{H}{\underset{H}{C}}-O-O$

(B)

We believe that this spectrum is a direct evidence for producing radicals by breaking bonds in the polymer by mechanical force.

Acknowledgments. Our grateful acknowledgment is due to the support of this work by the Korea Research Center for Theoretical Physics and Chemistry. We also express our sincere thanks to the Hannam Chemical Corporation (Seoul, Korea) who generously endowed the polystyrene samples.

References

(1) (a) A. V. Tobolsky, "Properties and Structure of Polymers," John Wiley & Sons Inc., 1960, Chap. 5; (b) A. Casale, R. S. Porter and J. F. Johnson, *Rubber Chem. and Technol.*, **44**, 534 (1971).

(2) J. F. S. Yu, J. L. Zakin and G. K. Patterson, *J. Appl. Polym. Sci.*, **23**, 2493 (1979).

(3) T. Ree and H. Eyring, *J. Appl. Phys.*, **26**, 793 (1955).

(4) (a) H. Eyring, *J. Chem. Phys.*, **4**, 283 (1936); (b) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," p. 480–484, McGraw-Hill Comp., New York, 1942.

(5) T. Ree and H. Eyring, *J. Appl. Phys.*, **26**, 800 (1955).

(6) M. Sakaguchi and J. Sohma, *J. Polym. Sci., Polym. Phys. Ed.*, **13**, 1233 (1975).

(7) J. R. Van Wazer, J. W. Lyons, K. Y. Kim and R. E. Colwell, "Viscosity and Flow Measurement," p. 219, Interscience Publishers, New York, 1963.

(8) J. Brandrup and E. H. Immergut, "Polymer Handbook," 2nd Ed., John Wiley, New York, 1975, p.N–17.

(9) (a) Ref. 4(b) p. 500; (b) Ref. 5; (c) T. Ree, "Theory of Non-Newtonian Flow," in "Symposium for High Polymer Physics," p. 43, Published by the Center for Theoretical Physics and Chemistry, Seoul, Korea, 1975.

(10) (a) T. Ree and H. Eyring, *Textile Res. J.*, **21**, 789, 799 (1951); (b) M. Chen, T. Ree and H. Eyring, *ibid.*, **22**, 416 (1952); (c) T. Ree, S. Hahn and H. Eyring, "Proceeding of International Wool Textile Research Conference," p. D234 Australia, 1955; (d) S. Hahn, H. Eyring, I. Higuch and T. Ree, *J. Natl. Grease Inst. (Spokesman)*, **22**, 121 (1958); (e) S. Hahn, T. Ree and H. Eyring, "Noncrystalline Solides," Ed. V. P. Fréchette. p. 297, John Wiley, New York, 1960.

(11) B. Ranby and J. F. Rabek, "EPR Spectroscopy in Polymer Research," p. 284 Springer-Verlag, Berlin, 1977.

(12) B. H. J. Bielski and J. M. Gebicki, "Atlas of Electron Spin Resonance Spectra", p. 492, Academic Press, New York, 1967.

Determination of Reactivity by MO Theory (XX). An MO Theoretical Study on Mechanism of Thiocarbonyl Addition.

Ikchoon Lee† and Kiyull Yang

Department of Chemistry, Inha University, Inchon 160 (*Received june 24, 1981*)

Ab initio molecular orbital calculations have been performed in an effeort to determine which types of chemical interactions play essential roles for the system, OH^-+CH_2S, $H_2O+CH_2SH^+$, and H_2O+CH_2S. The most important contribution to the interaction energy in controlling reaction path is the exchange repulsion energy, EX, which is largely responsible for the shape of the total interaction energy curve. In the ion-molecule reaction, prior protonation of thioformaldehyde or prior deprotonation of water leads to formation of the corresponding ionic adducts ($H_2\overset{+}{O}CH_2SH$ and $HOCH_2S^-$), with no barrier to reaction, simulating specific acid and base catalysis, respectively, as in the case of formaldehyde. Otherwise, approach of water to thioformaldehyde gives rise to a completely repulsive interaction.

Introduction

Nucleophilic substitution mechanisms on a carbonyl carbon have been studied extensively[1]. It has been shown theoretically[2] as well as experimentally[3] that a nucleophile attacks the carbonyl π-orbital from above and slightly rear of the carbonyl carbon and proceeds via a tetrahedral intermediate.

In this work characteristics of thiocarbonyl hydration mechanism have been studied using a simplest thiocarbonyl