and below, the temperature of precipitation, these adducts were not liquid crystalline. As is true for the uncomplexed polymers, the adducts did not exhibit well-defined melting points. Instead, the last two produced softened systems at ~280 °C. Gradual decomposition of these polymers was noted when they were kept at ~280 °C, leading us not to test the modest molecular weight poly(*p*-phenylene terephthalamide) we had on hand. In all cases, the diacid could be removed from the adducts by dissolution.

The structures which are most reasonable for these adducts have the common features of a diacid forming a total of four hydrogen bonds with two parallel, oppositely oriented polyamide chains. Detailed crystal structures and understanding of the molecular packing will have to wait better-formed samples. Two points are likely to be of particular interest. Models indicate that the carbonyl–hydroxyl pair may adopt a cis orientation in the adduct, unlike the conformation found in acid-monomeric amide complexes.[5] The open spaces introduced between consecutive diacids in a plane may imply perpendicular arrays of complexed polyamide and diacid in the crystalline adduct.

### References and Notes

(1) Partially crystalline adducts of poly(alkylbenzimidazole) polymers with strong acids have been prepared: Adrova, N. A.; Koton, M. M.; Dubnova, A. M.; Moskvina, Y. M.; Pokrovski, Y. I.; Fedorova, Y. F. *Polym. Sci. USSR (Engl. Transl.)* **1965**, *7*, 335. Ginsburg, B. M.; Korzhavin, L. N.; Frenkel, S. Y.; Laius, L. A.; Adrova, N. A. *Ibid.* **1966**, *8*, 302. Aharoni, S. M. *J. Appl. Polym. Sci.* **1977**, *21*, 181. Poly(ethylene oxide) and mercuric chloride form a 4:1 complex. Iwamoto, R.; Saito, Y.; Ishihara, H.; Tadokoro, H. *J. Polym. Sci., Part A-2* **1968**, *6*, 1509.

(2) See, for example: "The Structure and Action of Proteins"; Dickerson, R. E., Geis, I., Eds.; Harper and Row: New York, 1969.

(3) Bates, T. H.; Stockmayer, W. H. *Macromolecules* **1968**, *1*, 12, 17.

(4) Acierno, D.; La Mantia, F. P.; Polizzotti, G.; Ciferri, A. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1903. Kim, H.; Harget, P. J. *J. Appl. Phys.* **1979**, *50*, 6072.

(5) Leiserowitz, L.; Nader, F. *Acta Crystallogr., Sect. B* **1977**, *33*, 2719.

**S. M. Aharoni* and E. Wasserman**

*Corporate Research and Development*
*Allied Chemical Corporation*
*Morristown, New Jersey 07960*

*Received November 11, 1980*

---

## On the Material Time Constant Characterizing the Nonlinear Viscoelasticity of Entangled Polymeric Systems

In previous papers,[1,2] we have seen that the nonlinear behavior of concentrated polymer solutions can be well described by the Doi–Edwards theory[3] at times longer than a certain value $\tau_k$, empirically determined for each solution, in the stress relaxation process. It has also be shown on the basis of a few available data that the quantity $\tau_k$ is related to the number of entanglements per molecule, $M/M_e$, through the simple relation[1]

$$\tau_1{}^0/\tau_k \simeq M/M_e \tag{1}$$

where $\tau_1{}^0$ is the maximum relaxation time for the stress relaxation. In eq 1, $M$ represents the molecular weight and $M_e$ the molecular weight of the polymer chain between entanglements. Here we study $\tau_k$ over wide ranges of molecular weight and concentration and try to find its molecular-theoretical interpretation in view of the Doi–Edwards theory.

The Doi–Edwards theory is based on the tube model of de Gennes for entangled polymeric systems[4] and involves two characteristic times first proposed by de Gennes. One denoted as $T_{eq}$ is the equilibration time of the fluctuation of contour length of a polymer chain confined in a tube. The other, $T_d$, represents the time for a chain to change shape completely through disengaging from a tube in which it is initially confined. In the Doi–Edwards version of the theory,[3,5] the quantitites $T_{eq}$ and $T_d$ are proportional to the second and the third power, respectively, of the number of entanglements per molecule. It is predicted that the stress at times sufficiently longer than $T_{eq}$ following the application of stepwise strain should be factored into a function of time and one of magnitude of strain. The theory predicts also that the maximum relaxation time of the stress, $\tau_1{}^0$, should be equal to $T_d$.

For stepwise shear deformations of polystyrene solutions, each of the stress components, i.e., the shear and normal stresses, could be factored into a function of time $t$ and one of the magnitude of shear $\gamma$ at times longer than a certain value $\tau_k$ determined for each solution.[1,2] The function representing the strain dependence of each stress component was in close agreement with that given by the Doi–Edwards theory. Equation 1 approximately represented the effects of molecular weight and concentration on $\tau_k$ evaluated from the then available data; the quantity $M_e$ was evaluated from the relation

$$cM_e = 2 \times 10^4 \text{ g cm}^{-3} \tag{2}$$

where $c$ is the concentration. One may suppose that eq 1 is in accord with the prediction of the Doi–Edwards theory that $T_d/T_{eq} \propto M/M_e$ under the plausible assumption that $\tau_k$ is a measure of the time sufficiently longer than $T_{eq}$ and is a constant multiple of $T_{eq}$.

On the other hand, it is well-known that the maximum relaxation time $\tau_1{}^0$ of polymer concentrates is approximately proportional to $M^{3.5}$ instead of $M^{3.0}$, the theoretical prediction. Thus we will be led to the relation

$$\tau_1{}^0/\tau_k \propto (M/M_e)^{1.5} \tag{3}$$

in place of eq 1, if we assume that $T_{eq}$ is still proportional to $(M/M_e)^2$ and that $\tau_k$ is a constant multiple of $T_{eq}$. The tentative relation (1) is inconsistent with these assumptions. Incidentally the line below eq 16 of ref 1 is in error. It should be corrected as "Equations 4 and 5 lead to ...".

In order to investigate the detailed properties of $\tau_k$, we measured the shear stress in a stepwise shear strain for a few polystyrene solutions. The polystyrene samples were the standard polystyrenes from Pressure Chemical Co. Molecular weights of the polymers, $M$, were $9.50 \times 10^5$ (lot no. 61208), $6.70 \times 10^5$ (no. 13a), and $2.33 \times 10^5$ (no. 50124). The solvent was a chlorinated biphenyl, Aroclor 1248, from Monsanto Chemical Co. Seven solutions were tested. The concentrations $c$ are listed in Table I together with the methods of stress measurements and the results on $\tau_1{}^0/\tau_k$. For solutions of relatively low viscosities, the shear stress was measured with a relaxommeter of the cone-and-plate type,[6] represented by CP in Table I. For solutions of high viscosities, the stress was measured with a tensile tester,[7] represented by TT in Table I. In this case the sample was held between two parallel glass plates and the two plates were pulled in opposite directions with the tensile tester. Measurements were performed for magnitudes of shear $\gamma$ ranging from 0.5 to 4. All the measurements were performed at 30 °C. The ratio $\tau_1{}^0/\tau_k$ was determined through comparison of the shape of curves for various $\gamma$ values on

456 *Macromolecules* **1981,** *14,* 456-458

**Table I**
**$\tau_1^0/\tau_k$ for Polystyrene Solutions**

| $M$ | $c$, g cm$^{-3}$ | solvent[a] | method[b] | $\tau_1^0/\tau_k$ | ref |
|---|---|---|---|---|---|
| $2.33 \times 10^5$ | 0.40 | CB | CP | 1.55 | *c* |
| | 0.50 | CB | TT | 2.0 | *c* |
| $6.70 \times 10^5$ | 0.30 | CB | CP | 3.5 | *c* |
| | 0.40 | CB | TT | 6.7 | *c* |
| $9.50 \times 10^5$ | 0.20 | CB | CP | 3.0 | *c* |
| | 0.30 | CB | TT, CP | 7.5 | *c* |
| | 0.40 | CB | TT | 11 | *c* |
| $1.80 \times 10^6$ | 0.276 | CB | CP | 24 | *d* |
| $5.60 \times 10^6$ | 0.221 | DEP | CP | 54 | *d* |
| $7.60 \times 10^6$ | 0.176 | DEP | CP | 65 | *d* |
| | 0.221 | DEP | CP | 86 | *d* |

[a] CB stands for chlorinated biphenyl and DEP for diethyl phthalate. [b] CP stands for the method using a cone-and-plate type relaxometer and TT the method utilizing the tensile tester as explained in text. [c] Present study. [d] Reference 4.

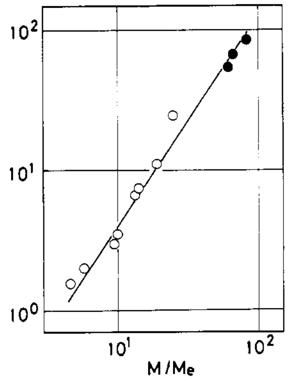

**Figure 1.** $\tau_1^0/\tau_k$ plotted against $M/M_e$, the number of entanglements per molecule for polystyrene solutions. Filled circles are for solutions in diethyl phthalate and unfilled circles in chlorinated biphenyl. Slope of line is 1.5.

the graph where the shear stress was plotted against time with log-log scales.[1] The values of $\tau_1^0$ and $\tau_k$ are not separately shown in Table I. These values were much affected by the slight error in concentration that was caused by the long waiting time to eliminate bubbles from the sample. The variation of the ratio $\tau_1^0/\tau_k$ with the slight change of concentration was negligible: The same value was obtained for different batches of the solution. Table I also includes the results reported previously.[1]

The ratio $\tau_1^0/\tau_k$ is plotted against $M/M_e$ with log-log scales in Figure 1. Here $M_e$ was determined with eq 2. The unfilled circles represent the solutions in chlorinated biphenyl and the filled circles in diethyl phthalate. The line is drawn with a slope 1.5. Obviously most of the data points lie close to the solid line. We may conclude that the tentative equation (1) should be replaced with (3). The previous conclusion was based on the four points at the top of the figure and was affected too much by the fourth point from the top. The present result implies that the quantity $\tau_k$ is proportional to $(M/M_e)^2$ and hence it may be closely related to the quantity $T_{eq}$ derived from the tube model theory.

One may dispute the appropriateness of eq 2. Several theories support the relation that[3,8]

$$M_e \propto c^{-a} \qquad a > 1 \tag{4}$$

at relatively low concentrations. However, one may presume that $M_e \propto c^{-1}$ at high concentrations.[8] Thus it may be plausible to use eq 2, which approximately represents many experimental data,[9] for the present solutions with relatively high concentrations. Experiments at lower concentrations will be necessary to investigate the appropriateness of eq 4.

## References and Notes

(1) Osaki, K.; Kurata, M. *Macromolecules* **1980,** *13,* 671.
(2) Osaki, K.; Kimura, S.; Kurata, M. *J. Polym. Sci., Polym. Phys. Ed.,* in press.
(3) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978,** *74,* 1789, 1802.
(4) de Gennes, P. G. *J. Chem. Phys.* **1971,** *55,* 572.
(5) Doi, M. *J. Polym. Sci., Polym. Phys. Ed.* **1980,** *18,* 1005.
(6) Tamura, M.; Kurata, M.; Osaki, K.; Einaga, Y.; Kimura, S. *Bull. Inst. Chem. Res., Kyoto Univ.* **1971,** *49,* 43.
(7) Kimura, S.; Osaki, K.; Kurata, M. *J. Polym. Sci., Polym. Phys. Ed.,* in press.
(8) Doi, M. *J. Phys. A: Math., Nucl. Gen.* **1975,** *8,* 959.
(9) Graessley, W. W. *Adv. Polym. Sci.* **1974,** *16,* 1.
(10) Present address: Japan Synthetic Rubber Co., Ltd., Yokkaichi, Mie 510, Japan.

**Kunihiro Osaki,* Shinichi Kimura,[10] Koji Nishizawa, and Michio Kurata**

*Institute for Chemical Research*
*Kyoto University*
*Uji, Kyoto 611, Japan*

*Received December 16, 1980*

## SAXS Studies of Segmented Polyether Poly(urethaneurea) Elastomers

Considerable efforts have been directed at understanding the structure-property relationships in many block and segmented copolymer systems. Much of this work has been undertaken on the segmented polyurethane and segmented poly(urethaneurea) systems as a result of their high commercial utilization. Of interest are the nature of the domain structure and the variation in morphological texture of these systems in bulk form that possess different composition or fabrication history.

In a series of recent papers the properties of segmented poly(urethaneureas) based on 2,4-TDI with poly(tetramethylene oxide), PTMO, as the soft segment and ethylenediamine as chain extender have been extensively studied by Sung and co-workers.[1-3] In general, considerable improvement in the extent of phase segregation was suggested by a much lower $T_g$ of the soft-segment phase and a much higher $T_g$ of the hard-segment domains in poly(urethaneureas) extended with ethylenediamine rather than with butanediol. IR spectra of two polyether poly(urethaneureas) with 1000 and 2000 molecular weight PTMO suggest the presence of three-dimensional hydrogen bonding within their hard-segment domains, where one urea carbonyl is bonded to two NH groups. The interface between the domain and the soft matrix was suggested to be quite sharp since most of the urethane carbonyl is free from bonding; i.e., unbonded carbonyl existed. In addition, mechanical properties implied that, at the same urea content (30% by weight of hard segment), the domains in the PTMO-1000 sample are more interconnected than those in the PTMO-2000 sample and that the soft-segment phase of the former may contain more solubilized hard segment than that of the latter.[2] That is, the PTMO-2000 sample was believed to exhibit better phase separation and consequently to account for better mechanical properties such as higher elongation to break, greater toughness, lower hysteresis, and a slower rate of stress relaxation, even though ultimate tensile strength is slightly lower. The current work investigates the morphology of these same urea-based urethanes by small-angle X-ray scattering and,

0024-9297/81/2214-0456$01.25/0