*Polym. Sci., Part C*, **23**, 365 (1968).
(22) F. A. Bovey, F. P. Hood, E. W. Anderson, and L. C. Snyder, *J. Chem. Phys.*, **42**, 3900 (1965).
(23) T. Yoshino, Y. Kikuchi, and J. Komiyama, *J. Phys. Chem.*, **70**, 1059 (1966).
(24) Y. Fujiwara, S. Fujiwara, and K. Fujii, *J. Polym. Sci., Part A-1*, **4**, 257 (1966).
(25) D. Doskočilová, J. Štokr, E. Votavova, B. Schneider, and D. Lim, *J. Polym. Sci., Part C*, **16**, 2225 (1967).
(26) T. Moritani and Y. Fujiwara, *J. Chem. Phys.*, **59**, 1175 (1973).
(27) A. R. Schultz, *J. Am. Chem. Soc.*, **76**, 3422 (1954).
(28) M. Matsumoto and Y. Ohyanagi, *J. Polym. Sci.*, **50**, S1 (1961).
(29) I. Sakurada and K. Fuchino, *Sci. Pap. Inst. Phys. Chem. Res. (Jpn.)*, **39**, 78 (1941); cited in ref 8, p 450.
(30) W. J. Dulmage, *J. Polym. Sci.*, **26**, 277 (1957).
(31) H. Chanzy and E. Roche, *J. Polym. Sci., Polym. Phys. Ed.*, **12**, 2583 (1974); **13**, 1859 (1975).
(32) E. Roche, H. Chanzy, M. Boudeulle, R. H. Marchessault, and P. R. Sundararajan, *Macromolecules*, submitted.
(33) A. Sarko and R. H. Marchessault, *Science*, **154**, 3757 (1966).
(34) R. H. Marchessault and P. R. Sundararajan, *Pure Appl. Chem.*, **42**, 399 (1975).

# Hypersonic Relaxation and the Glass–Rubber Relaxation in Poly(propylene glycol)

**G. D. Patterson,* D. C. Douglass, and J. P. Latham**

*Bell Laboratories, Murray Hill, New Jersey 07974.* *Received April 26, 1977*

ABSTRACT: Hypersonic relaxation in poly(propylene glycol) (PPG) was studied using Brillouin spectroscopy. The loss tan $\delta$ exhibited two maxima as a function of temperature. The higher temperature maximum at 100 °C agreed with recent[1] dielectric relaxation results on PPG at gigahertz frequencies. The secondary maximum at 50 °C agreed with previous hypersonic relaxation studies of PPG and fell on an extrapolation of the secondary glass–rubber relaxation data. NMR relaxation was also studied on the same sample. The $T_1$ minimum occurred at 270 K and the $T_{1\rho}$ minimum at 235 K. These results agreed with dielectric relaxation in the megahertz and kilohertz regions. No secondary glass–rubber relaxation was observed by NMR, but the rotation of methyl groups was detected.

Dielectric relaxation in poly(propylene glycol) (PPG) has been examined from just greater than $10^{-4}$ Hz to just less than $10^{10}$ Hz.[1-3] The loss maxima for the primary glass–rubber relaxation could be correlated[1] over the entire frequency range with an equation of the form

$$\log f = \log f_\infty - \frac{B}{T - T_0} \tag{1}$$

where $f_\infty$ is the extrapolated frequency at infinite temperature and $T_0$ is a temperature below the nominal $T_g$. In addition to the primary loss peak McCammon and Work[4] reported a weak secondary peak in the dielectric loss spectrum. The secondary relaxation has also been studied by dynamic mechanical methods.[5,6] The secondary main chain glass–rubber relaxation data can be correlated according to

$$\log f = \log f_\infty - \frac{B}{T} \tag{2}$$

Recent studies[7-9] of hypersonic relaxation in polymers using Brillouin spectroscopy have revealed that the temperatures of maximum loss determined by this technique agree with an extrapolation of the lower frequency secondary relaxation data according to eq 2. In most polymers the primary and secondary main chain glass–rubber relaxations are not resolved at $10^9$ Hz. Thus, only a single loss peak is observed by Brillouin scattering or dielectric relaxation at hypersonic frequencies. However, the temperature of maximum loss for PPG determined by Yano et al.[1] using dielectric relaxation is higher than the hypersonic results reported by Wang and Huang[10] and Lindsay et al.[11] The dielectric relaxation results[1] fit the extrapolated primary relaxation line. The observed hypersonic relaxation falls on a reasonable extrapolation of the limited secondary relaxation data.[4-6]

There is no reason to expect that hypersonic relaxation would be sensitive only to the secondary relaxation process in a region where the two relaxations could be resolved. However, the magnitude of tan $\delta$ at the two temperatures of maximum loss could be quite different. The failure of Yano et al.[1] to detect the secondary relaxation at gigahertz frequencies can easily be attributed to the very small dielectric loss associated with this process.

In the present work we reexamine hypersonic relaxation in poly(propylene glycol) using Brillouin spectroscopy. In addition, new data were obtained from nuclear magnetic relaxation (NMR) for PPG.

## Experimental Section

**Materials.** Poly(propylene glycol) of nominal molecular weight 4000 was obtained from Polysciences, Inc. It is important to choose the molecular weight to be high enough to obtain the limiting results for both the primary and secondary main-chain glass–rubber relaxations.[8] The fluid was filtered directly into a 1-cm square quartz fluorimeter cell for the Brillouin scattering experiments or into a 5-mm NMR tube for the nuclear magnetic relaxation experiments.

**Brillouin Scattering.** Brillouin spectra were obtained as described previously.[7-9] The incident wavelength was 5145 Å and the scattering angle was 90°. The free spectral range of the Fabry–Perot interferometer was 19.3 GHz. The spectra were recorded digitally with two orders in 1024 points. The observed Brillouin spectra were deconvoluted by comparing them with spectra calculated by convoluting the true instrumental function with the theoretical form for the Brillouin spectrum. For our interferometer this procedure resulted in subtracting the instrumental half-width at half-height from the observed Brillouin line widths since the transmission function was accurately given by an Airy function. Measurements of the Rayleigh–Brillouin spectrum were carried out from −10 to 170 °C. The loss tan $\delta$ was calculated according to

$$\tan \delta = (2\Gamma_l/\Delta\omega_l)(1 - (\Gamma_l/\Delta\omega_l)^2)^{-1} \tag{3}$$

The NMR data reported are obtained from longitudinal relaxation in the laboratory, $T_1$, and rotating frames, $T_{1\rho}$, by conventional 180–90° and spin-locking pulse sequencies, respectively.[12]

## Results and Discussion

The Brillouin splittings $\Delta\omega_l$ and line widths $\Gamma_l$ are listed as a function of temperature in Table I. The frequencies and tan $\delta$ are plotted vs. $T$ in Figure 1. The loss maximum at approximately 50 °C and 5.43 GHz is in good agreement with the previous results of Wang and Huang[10] and Lindsay et al.[11] In

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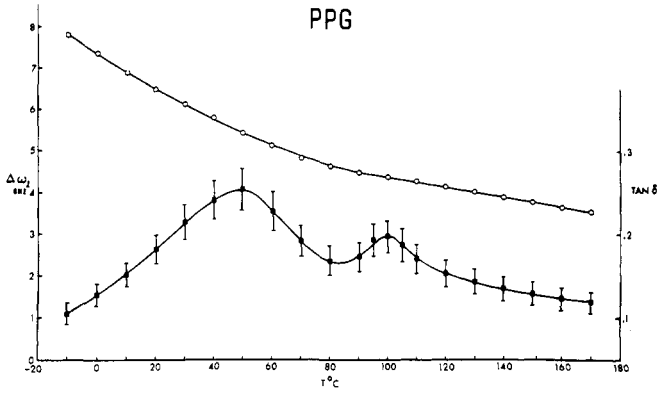


**Figure 1.** Brillouin splitting $\Delta\omega_1$ (in GHz) (○) and loss tan $\delta$ (■) are plotted vs. $T$ for poly(propylene glycol).

**Table I**
**Brillouin Splittings and Line Widths for PPG**

| $T$, °C | $\Delta\omega_1$, GHz | $\Gamma_1$, GHz |
|---|---|---|
| −10 | 7.80 ± 0.04 | 0.41 ± 0.04 |
| 0 | 7.36 ± 0.04 | 0.46 ± 0.04 |
| 10 | 6.98 ± 0.04 | 0.54 ± 0.04 |
| 20 | 6.57 ± 0.04 | 0.58 ± 0.04 |
| 30 | 6.13 ± 0.04 | 0.63 ± 0.04 |
| 40 | 5.80 ± 0.04 | 0.69 ± 0.04 |
| 50 | 5.43 ± 0.04 | 0.68 ± 0.04 |
| 60 | 5.13 ± 0.04 | 0.59 ± 0.04 |
| 70 | 4.90 ± 0.04 | 0.49 ± 0.04 |
| 80 | 4.73 ± 0.04 | 0.41 ± 0.04 |
| 90 | 4.55 ± 0.04 | 0.40 ± 0.04 |
| 95 | 4.47 ± 0.04 | 0.44 ± 0.04 |
| 100 | 4.40 ± 0.04 | 0.45 ± 0.04 |
| 105 | 4.32 ± 0.04 | 0.41 ± 0.04 |
| 110 | 4.26 ± 0.04 | 0.36 ± 0.04 |
| 120 | 4.14 ± 0.04 | 0.32 ± 0.04 |
| 130 | 4.02 ± 0.04 | 0.29 ± 0.04 |
| 140 | 3.90 ± 0.04 | 0.26 ± 0.04 |
| 150 | 3.79 ± 0.04 | 0.24 ± 0.04 |
| 160 | 3.68 ± 0.04 | 0.23 ± 0.04 |
| 170 | 3.57 ± 0.04 | 0.22 ± 0.04 |

addition there is a loss maximum at approximately 100 °C and 4.40 GHz. The higher temperature loss agrees very well with the dielectric results of Yano et al.[1]

The measurements of $T_1$ at 30 MHz are plotted vs. $1/T$ in Figure 2. The minimum at 270 K is due to the primary main-chain glass–rubber relaxation and agrees very well with the dielectric data in the meghertz region[1-3] and the previous NMR results of Connor et al.[13] The $T_1$ minimum at lower temperatures has been shown[13] to be due to the rotation of the methyl side groups. Measurements of $T_{1\rho}$ are plotted vs. $1/T$ in Figure 3. The minimum at 235 K agrees with the dielectric relaxation results[1-3] in the kilohertz region. The apparent minimum at very low temperature is again due to the methyl groups. However, no secondary main chain loss process was resolved by NMR.

A compilation of the dielectric relaxation,[1-4] dynamic mechanical,[5] and the present hypersonic and NMR relaxation results is presented in Figure 4. The log of the frequency is plotted vs. the reciprocal of the temperature of maximum loss to obtain a transition map. The primary and secondary main chain glass–rubber relaxation lines have not merged at high frequencies.

At low frequencies, the loss peaks observed by dielectric and mechanical relaxation are very sharp and half-widths at half-height of 2–5 °C are often seen. As the frequency is increased the width of the loss peaks also increases. In the gigacycle region, the observed width[1] of the plots of $\epsilon''$ vs. $T$ for the primary relaxation was greater than 50 °C. Thus it be-

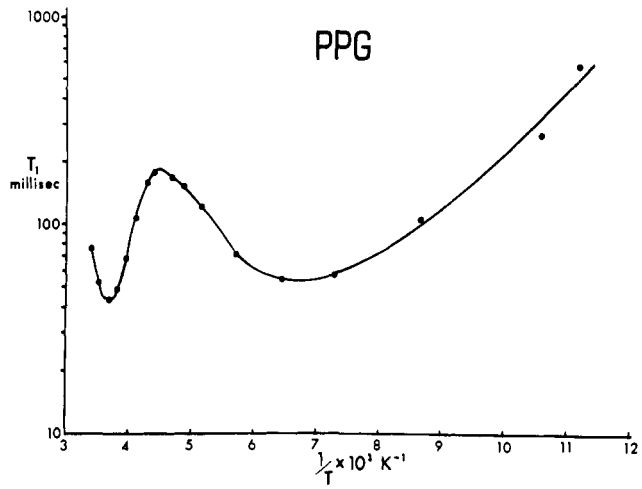


**Figure 2.** Relaxation time $T_1$ vs. $1/T$ for PPG.

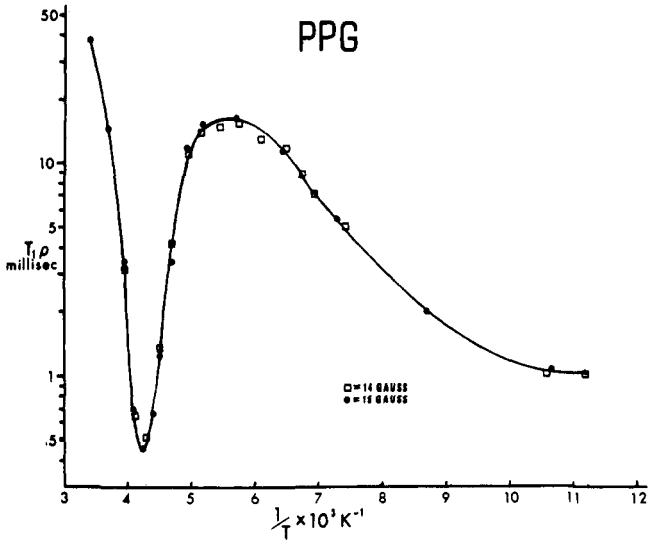


**Figure 3.** Relaxation time $T_{1\rho}$ vs. $1/T$ for PPG.

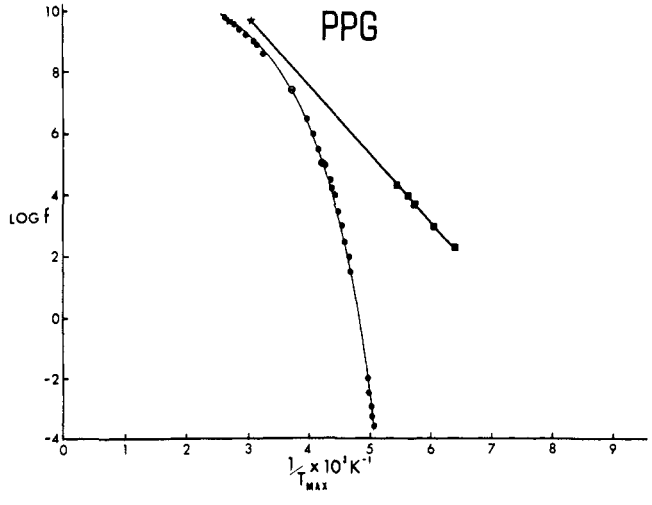


**Figure 4.** Transition map for PPG. The Brillouin results are indicated by ★ and the NMR results by ⊖. The other primary relaxation data are from ref 1–3. The other secondary data are from ref 4 and 5.

comes very difficult to detect a weak loss in this frequency range.

At low frequencies, the primary glass–rubber relaxation usually leads to a much larger mechanical loss than the secondary main-chain relaxation.[6] At hypersonic frequencies in PPG the secondary process dominates the loss spectrum. In PPG, it appears that hypersonic relaxation is the only technique that resolves the two processes at high frequencies. Both dielectric and magnetic relaxation were unable to detect the secondary relaxation in this frequency range.

Brillouin scattering can be carried out with all amorphous polymers which are reasonably colorless. Even more highly colored materials may be studied as films.[14] Thus it is a very general technique for studying mechanical relaxation at high frequencies. The resolution of both a primary and secondary loss peak in polymers other than PPG is being actively pursued.

## References and Notes


(1) S. Yano, R. R. Rahalkar, S. P. Hunter, C. H. Wang, and R. H. Boyd, *J. Polym. Sci., Polym. Phys. Ed.*, **14**, 1877 (1976).
(2) G. Williams, *Trans. Faraday Soc.*, **61**, 1564 (1965).
(3) M. E. Baur and W. H. Stockmayer, *J. Chem. Phys.*, **43**, 4319 (1965).
(4) R. D. McCammon and R. N. Work, *Rev. Sci. Instrum.*, **36**, 1169 (1965).
(5) J. M. Crissman, J. A. Sauer, and A. E. Woodward, *J. Polym. Sci., Part* A-2, 5075 (1964).
(6) R. G. Saba, J. A. Sauer, and A. E. Woodward, *J. Polym. Sci., Part A-1*, 1483 (1963).
(7) G. D. Patterson, *J. Polym. Sci., Polym. Phys. Ed.*, **15**, 455 (1977).
(8) G. D. Patterson, *J. Polym. Sci., Polym. Phys. Ed.*, **15**, 579 (1977).
(9) G. D. Patterson, *J. Macromol. Sci., Phys.*, **13**, 647 (1977).
(10) C. H. Wang and Y. Y. Huang, *J. Chem. Phys.*, **64**, 4847 (1976).
(11) S. M. Lindsay, A. J. Hartley, and I. W. Shepherd, *Polymer*, **17**, 501 (1976).
(12) G. P. Jones, D. C. Douglass, and D. W. McCall, *Rev. Sci. Instrum.*, **36**, 1460 (1965).
(13) T. M. Connor, D. J. Blears, and G. Allen, *Trans. Faraday Soc.*, **61**, 1097 (1965).
(14) G. D. Patterson, *J. Polym. Sci., Polym. Phys. Ed.*, **14**, 143 (1976).


# Macrocyclic Tetrahydrofuran Oligomers. 2.[1] Formation of Macrocycles in the Polymerization of Tetrahydrofuran with Triflic Acid


**G. Pruckmayr*[2] and T. K. Wu[3]**

*Industrial Chemicals Department and Plastic Products and Resins Department, E. I. du Pont de Nemours and Co., Inc., Experimental Station, Wilmington, Delaware 19898.*

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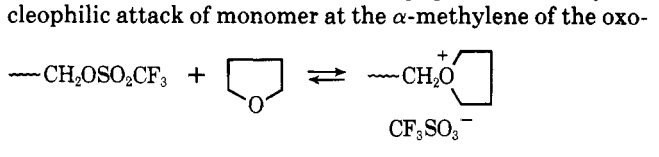
ABSTRACT: The formation of macrocyclic oligomers in tetrahydrofuran polymerization systems initiated with ethyl trifluoromethanesulfonate (ethyl triflate) and with trifluoromethanesulfonic acid (triflic acid) has been investigated. In polymerization systems initiated with ethyl triflate, linear and cyclic oligomers are found by gas chromatography/chemical ionization mass spectrometry. In systems initiated with triflic acid only cyclic oligomers are found under similar polymerization conditions. From these findings, as well as from conversion and solution viscosity data, a chain coupling–ring opening mechanism is discussed for the polymerization of tetrahydrofuran with triflic acid.


The mechanism of the polymerization of tetrahydrofuran (THF) has been investigated recently in great detail,[4,5] particularly the polymerization initiated with esters of trifluoromethanesulfonic acid (triflic acid).[6–9] An equilibrium between an oxonium ion and a covalent ester at the propagating chain head was found to depend on the polarity of the medium: In a medium of high polarity, the propagating species was the expected oxonium ion. In a medium of low polarity, the predominant end group was found to be a covalent ester, formed by attack of the counterion at the $\alpha$-methylene carbons of the oxonium ion.[10] Chain propagation occurs by nucleophilic attack of monomer at the $\alpha$-methylene of the oxo-



nium ion or the ester to form a new oxonium ion, which may subsequently again be ring opened by the counterion.

A series of polymerization $\rightleftarrows$ depolymerization equilibria thus exist in such a system, and one would expect the formation of at least some macrocyclic oligomers through "backbiting" reactions. Such macrocycles have indeed been found recently. In a previous publication, we reported the identification of "THF crown ethers", formed during the polymerization of tetrahydrofuran (THF) with trialkyl oxonium salts.[1] We now wish to report the identification of such crown ethers in THF polymerizations initiated by alkyl triflate and triflic acid.

The mechanistic implications of crown ether formation in acid-catalyzed polymerizations are discussed, and a possible mechanism for such polymerizations is proposed.

## Experimental Section

Dry tetrahydrofuran stored over metallic sodium was used as the monomer. Trifluoromethanesulfonic acid was distilled under $N_2$ at atmospheric pressure prior to use (bp 160 °C). All other reagents or solvents are commercially available in reagent grade and were used without further purification.

Polymerizations were carried out by weighing reactants and solvent into 15-cm Pyrex polymerization tubes sealed with rubber serum caps. For example, 10.0 g of THF and 3.5 g of $CD_3NO_2$ were mixed in a polymerization tube, and 0.9 g (0.53 mL) of $CF_3SO_3H$ was added through the septum with a 1-mL syringe. The reactants were mixed thoroughly for 10 s on a mechanical vortex shaker, and the polymerization tube was immediately placed into a constant temperature bath. Samples were withdrawn periodically through the serum cap. The constant temperature bath, used for polymerizations and viscosity measurements, controlled the temperature to ±0.2 °C.

Viscosities were determined in Ostwald viscometer tubes, which were equipped with drying tubes, loosely packed with Aquasorb to prevent access of atmospheric moisture. Standard volumes (10 mL) of the polymerization mixtures were injected into the viscometer tubes and flow times measured to the closest 0.1 s.

Conversions and degrees of polymerization were calculated from 100 or 220 MHz NMR spectra, using the intensities of the monomer

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