(19) D. Chan, D. T. Mitchell, B. W. Ninham, and L. R. White, *J. Chem. Soc., Faraday Trans. 2*, **71**, 235 (1975).
(20) J. M. H. M. Scheutjens and G. J. Fleer, *J. Phys. Chem.*, **83**, 1619 (1979).
(21) R. R. Stromberg, D. J. Tutas, and E. Passaglia, *J. Phys. Chem.*, **69**, 3955 (1965).
(22) H. Gebhard and E. Killmann, *Angew. Makromol. Chem.*, **53**, 171 (1976).
(23) F. Patat, E. Killmann, and C. Schliebener, *Adv. Polym. Sci.*, **3**, 332 (1964).
(24) F. R. Eirich, *J. Colloid Interface Sci.*, **58**, 423 (1977).
(25) F. W. Rowland and F. R. Eirich, *J. Polym. Sci., Part A-1*, **4**, 2401 (1966).
(26) E. Pefferkorn, P. Dejardin, and R. Varoqui, *J. Colloid Interface Sci.*, **63**, 353 (1978).
(27) B. J. Fontana and J. R. Thomas, *J. Phys. Chem.*, **65**, 480 (1961).
(28) C. V. Linden and R. V. Leemput, *J. Colloid Interface Sci.*, **67**, 48 (1978).
(29) W. H. Grant, L. E. Smith, and R. R. Stromberg, *Discuss. Faraday Soc.*, **No. 59**, 205 (1976).
(30) A. Takahashi, M. Kawaguchi, and T. Kato, *Polym. Sci. Technol., Ser. B*, **12**, 729 (1980).
(31) F. L. McCrackin, *NBS Tech. Note (U.S.)*, 479 (1966).
(32) F. L. McCrackin and J. P. Colson, *NBS Spec. Publ. (U.S.)*, **No. 256** (1964).
(33) C. A. J. Hoeve, *J. Polym. Sci., Part C*, **No. 34**, 1 (1971).
(34) C. C. Berry, *J. Chem. Phys.*, **44**, 4550 (1966).
(35) K. Motomura and R. Matsuura, *J. Chem. Phys.*, **50**, 1281 (1969).
(36) A. T. Clark and M. Lal, *J. Chem. Soc., Faraday Trans. 2*, **74**, 1857 (1978).
(37) R. I. Feigin and D. H. Napper, *J. Colloid Interface Sci.*, **71**, 117 (1979).

Ultrasonic Relaxation in Aqueous Solutions of Dextran

Shigeo Kato,* Tatsuya Suzuki, Hiroyasu Nomura, and Yutaka Miyahara

Department of Chemical Engineering, Faculty of Engineering, Nagoya University, Nagoya 464, Japan.

Received July 6, 1979

ABSTRACT: The ultrasonic absorption coefficients of aqueous solutions of dextran and some saccharides have been measured in a frequency range from 0.8 to 130 MHz and over a temperature range from 10 to 35 °C. In all solutions of dextran two relaxation processes are observed within the frequency range examined, which have relaxation frequencies at about 1 and 12–15 MHz. They are likely independent of molecular weight and temperature. However, the aqueous solutions of saccharides do not exhibit any relaxation. The relaxation processes observed in aqueous solutions of dextran are considered to be volume relaxations due to the segmental motion of the polymer chain. The most likely origin of the volume relaxations is the exchange process of the hydrated water molecules in the hydration sphere of the polymer.

The solution properties of dextran have been investigated by a variety of methods, including viscosity, light scattering, and sedimentation.[1-3] However, the information obtained by these methods cannot reveal the "dynamical" properties of aqueous solutions of dextran.

The ultrasonic relaxation method has proved to be a powerful and efficient tool for investigating the dynamics of molecular processes such as conformational changes associated with polymer chains in the time range of 10^{-5}–10^{-10} s.[4,5]

The ultrasonic relaxation in aqueous solutions of dextran was first reported by Hawley and Dunn about 10 years ago.[6] Their study was very suggestive for the understanding of the relaxation mechanism of aqueous solutions of dextran. However, their measurement was carried out at 20 °C only, and the volume of data in the frequency range below 10 MHz was not sufficient for detailed discussion of the relaxation mechanism.

As was mentioned in our previous paper,[7] the data below 10 MHz are particularly important for discussion of the chain dynamics of stiff polymers such as cellulose acetate and dextran, and the ultrasonic absorption should be measured accurately as a function of temperature over a wide frequency range.

In this paper, we report accurate measurements of ultrasonic absorption of aqueous solutions of dextran at different temperatures, together with those of some saccharides. We discuss the possible mechanisms of the relaxation process in aqueous solutions of dextran with reference to the results on aqueous solutions of some saccharides.

Experimental Section

Materials. The dextran samples (1,6-poly(anhydroglucose)) used were supplied by Pharmacia Fine Chemical Co., Ltd. Molecular weight and the ratio of M_w/M_n of the samples are summarized in Table I. The samples of saccharides, glucose, maltose, and raffinose used were commercial extrapure grade reagents.

Table I
Molecular Weights and Intrinsic Viscosities of Dextran Samples

sample	M_w	M_n	M_w/M_n	$[\eta]^a$
T-10	9.4×10^3	5.3×10^3	1.71	0.096
T-40	4.0×10^4	3.0×10^4	1.33	0.21
T-110	1.1×10^5	7.6×10^4	1.44	0.32
T-2000	2.0×10^6			0.70

[a] At 20 °C.

Ultrasonic Absorption Measurements. The ultrasonic absorption coefficient, α (neper cm^{-1}), was measured by using a standard-pulse apparatus in the frequency range of 15–130 MHz. In the low-frequency range, 0.8–8 MHz, α was measured by a cylindrical resonator method. Two types of resonators were used in this work: one had a 1.65-mm path length and paired 2-MHz x-cut crystals having a 50-mm diameter, and the other had a 0.83-mm path length and 5-MHz x-cut crystals having a 30-mm diameter. A more detailed description of the apparatus and the experimental procedures have been published elsewhere.[7]

Distilled water was used as the reference material for the resonator method.

Sound Velocity and Density Measurements. The ultrasonic velocity was mainly measured with an interferometer working at a fixed 4.000-MHz frequency and occasionally with the cylindrical resonators. The density was measured with an Ostwald-type pycnometer of 20-mL capacity.

All measurements were carried out on freshly prepared solutions to avoid the aging effect. According to Hawley and Dunn,[6] the ultrasonic absorption of aqueous solutions of dextran varies linearly with concentration up to 10% throughout the molecular weight and frequency ranges. Therefore all the measurements were carried out at a constant concentration of 5.00 g/100 mL.

0024-9297/80/2213-0889$01.00/0

Table II
Relaxation Parameters for Aqueous Solutions of Dextran T 2000

t, °C	$10^{17}A_1$, nepers s^2 cm^{-1}	f_{r1}, MHz	$10^{17}B$, nepers s^2 cm^{-1}	f_{r2}, MHz	$10^{17}A_2$, nepers s^2 cm^{-1}	C, ms^{-1}	$10^3\mu_1$(max)	$10^3\mu_2$(max)
10	317	0.74	72.5	12.8	42.0	1460	0.167	0.678
15	162	1.0	54.7	16.3	33.1	1479	0.120	0.659
20	121	1.1	42.0	12.4	30.7	1493	0.100	0.363
25	107	1.0	40.0	12.0	27.0	1511	0.084	0.363
30	94.5	1.0	31.4	13.8	23.1	1520	0.072	0.329
35	61.6	1.0	29.0	12.4	21.4	1530	0.047	0.275

Table III
Relaxation Parameters for Aqueous Solutions of Dextran

sample	t, °C	$10^{17}A_1$, nepers s^2 cm^{-1}	f_{r1}, MHz	$10^{17}A_2$, nepers s^2 cm^{-1}	f_{r2}, MHz	$10^{17}B$, nepers s^2 cm^{-1}	C, ms^{-1}	$10^3\mu_1$(max)	$10^3\mu_2$(max)
T-10	10	52.0	1.4	46.0	13.0	42.5	1462	0.053	0.437
	15	49.0	1.2	42.5	14.0	33.5	1480	0.044	0.440
	20	26.1	1.6	25.0	15.0	30.9	1496	0.031	0.280
	25	26.4	1.3	21.0	15.0	27.1	1508	0.026	0.243
	30	11.5	1.5	19.0	15.0	23.5	1521	0.013	0.217
	35			16.7	14.0	21.4	1532		0.179
T-40	20	121	0.9	42.0	12.0	31.5	1494	0.081	0.389
T-110	20	121	1.0	42.0	12.4	31.3	1494	0.090	0.389

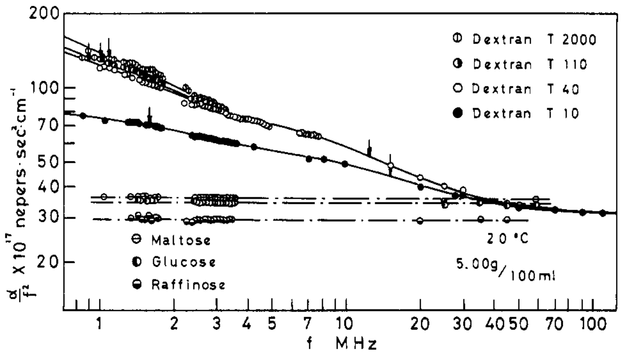

Figure 1. α/f^2 vs. frequency for aqueous solutions of dextran and some saccharides at 20 °C. The arrows represent the relaxation frequencies. The solid lines were calculated by eq 1.

Results

The values of sound velocity and density of aqueous solutions of dextran were in good agreement with those reported previously.[14] The variation of ultrasonic absorption, α/f^2, with frequency, f, was measured for aqueous solutions of dextran and saccharides.

Figure 1 shows the results expressed as α/f^2 vs. logarithmic frequency, log f, for aqueous solutions of dextran and saccharides at 20 °C. In all solutions of dextran, at least two relaxation processes were observed within the frequency range examined. However, the aqueous solutions of saccharides did not exhibit any relaxation. The solid lines in Figure 1 were drawn following the equation for double-relaxation processes

$$\frac{\alpha}{f^2} = \frac{A_1}{1+(f/f_{r1})^2} + \frac{A_2}{1+(f/f_{r2})^2} + B \tag{1}$$

f_{r1} and f_{r2} represent the relaxation frequencies and A_1, A_2, and B are relaxation parameters. Figure 2 shows similar plots for aqueous solutions of dextran T-2000 as a function of temperature. Figure 3 shows the relationship between absorption per wavelength, μ ($=\alpha\lambda$), and logarithmic frequency for aqueous solutions of dextran T-10 as a function of temperature.

As is seen in Figures 1–3, all experimental results of dextran solutions can be expressed by eq 1 within 3% deviation in the observed frequency range. Tables II and III summarize the values of relaxation parameters in eq 1. The two relaxation frequencies are located at about 1 MHz and 12–15 MHz, and they are independent of temperature. Furthermore, it seems likely that they are independent of molecular weight for molecular weight higher than 4 × 10^4. For the solution of dextran T-10, the relaxation frequencies are located at a slightly higher frequency than those of other solutions of dextran.

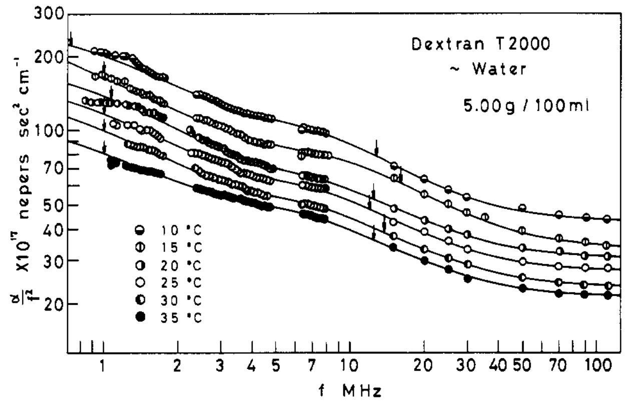

Figure 2. α/f^2 vs. frequency for aqueous solutions of dextran T-2000 at various temperatures. The arrows represent the relaxation frequencies. The solid lines were calculated by eq 1.

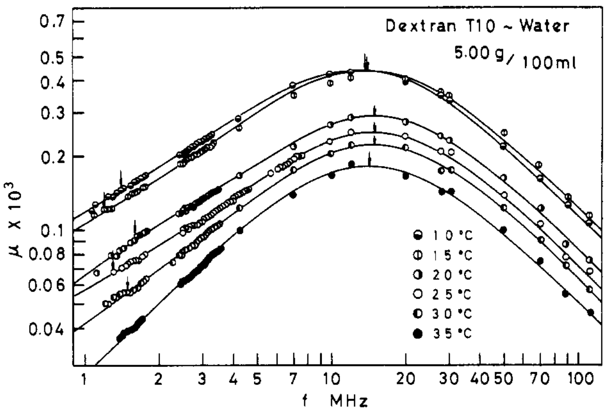

Figure 3. Absorption per wavelength, μ, vs. frequency for aqueous solutions of dextran T-10 at various temperatures. The arrows represent the relaxation frequencies. The solid lines were calculated by eq 1.

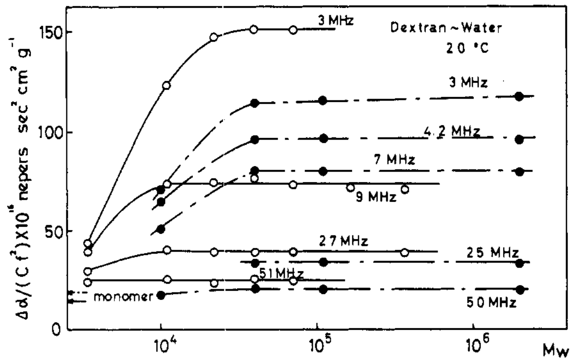

Figure 4. Dependence of $\Delta\alpha/f^2$ on molecular weight at various frequencies (○ is the data of Hawley and Dunn[6]).

To compare our results with Hawley's, the molecular weight dependence of $\Delta\alpha/f^2C$ in aqueous solutions of dextran at various frequencies is given in Figure 4. Here, $\Delta\alpha$ represents the absorption difference between that of solution and solvent and C is the concentration (g/100 mL). As is seen in Figure 4, our results are in good agreement with Hawley's at higher frequencies, but below 9 MHz their results are larger than ours. This disagreement may be due to their poor correction for the diffraction effect of sound absorption. As is well-known, the diffraction correction must be applied to the results of the absorption coefficient measured by the pulse method. The amount of this correction occupies such a large portion in the absorption coefficient observed at a few MHz that it makes the value of the absorption coefficient quite unreliable, especially when the solution has low attenuation. On the contrary, as has been already mentioned in our previous paper,[7] a cylindrical resonator method yields directly the excess absorption per wavelength, μ_{excess}, and it gives more reliable values of the absorption coefficient.

Discussion

No relaxation is observed in aqueous solutions of saccharides. For aqueous solutions of dextran, the relaxation parameters at the high-frequency limit, B, are nearly equal to the ultrasonic absorption coefficients of aqueous solutions of saccharides. These facts indicate that an ultrasonic relaxation process associated with a unit smaller than dextran consisting of three glucose units is observed at the frequencies about 100 MHz. Therefore, the relaxation processes observed should be attributed to the molecular motions of polymer chains in aqueous solutions of dextran.

Gettins et al.[8] observed the ultrasonic relaxation in agarose gels and considered that the origin of the relaxation was associated with either the interaction of the junction zones or their aggregates. Although dextran has a similar chemical structure to that of agarose, no gelation has been observed in this experiment over the whole temperature range. Therefore, the relaxation mechanism operation in agarose gels is not applicable to the relaxation process observed in dextran solutions.

The ultrasonic relaxation observed should be attributed to the molecular motion of polymer chains in dilute solution. Among the possible mechanisms for the ultrasonic relaxation, either of the following two are most plausible: (i) a process related to the normal mode motion of lower order of Rouse–Zimm type; (ii) a process described by the normal mode motion of higher order on the basis of the internal viscosity[9-11] or by the local mode model in polymer chains.[4,12,17]

In mechanism i the relaxation times should show strong molecular weight dependence, and using Zimm's theory,[18] one can estimate the relaxation times of the normal mode motion of lower order. Table IV summarizes the estimated relaxation times for aqueous solutions of dextran. Comparison of the calculated values with the relaxation frequencies observed clearly shows that the experimental results do not support mechanism i.

Table IV
Estimated Relaxation Times of Normal Motions

sample	relaxation time, s	
	$p^a = 1$	$p^a = 2$
T-10	1.62×10^{-8}	5.14×10^{-9}
T-40	1.38×10^{-7}	4.36×10^{-8}
T-110	4.88×10^{-7}	1.55×10^{-7}
T-2000	2.43×10^{-3}	7.71×10^{-4}

[a] p is the order of the normal mode motion in Zimm's theory.[18]

Two types of explanations have been used to interpret the molecular-weight-independent ultrasonic relaxation observed in various dilute polymer solutions. One is the normal-mode explanation using the internal viscosity.[9-11] The other is the description on the basis of a physical model.[4,12,17] The former is expressed more mathematically than the latter, but direct comparison of the expression with experimental results is very difficult. The latter is mathematically less rigorous, but it is so simple and intuitive that direct comparison can be easily done.

We feel that both models express, essentially, the same mechanism from the different points of view, so the difference of the two descriptions has little importance at this stage.

For simplicity, we will explain the present results with the physical model.

In general, the ultrasonic relaxation strength r can be written as[13]

$$r = \frac{(\gamma - 1)(C_p - C_{p\infty})}{C_p}\left\{1 - \frac{\Delta\bar{V}}{\Delta H}\,\frac{C_p}{\bar{V}\theta}\right\}^2 \qquad (2)$$

where γ and θ represent the ratio of specific heats (C_p/C_v) and expansibility, respectively. C_p is the specific heat at constant pressure, and C_v is that at constant volume. The subscript ∞ represents the value in the limit of high frequency. V is the molar volume, ΔV is the volume change associated with the relaxation process, and ΔH is the enthalpy change. As is seen in eq 2, the relaxation process can be divided into two cases: if the assumption $(\Delta V/\Delta H)(C_p/V\theta) \ll 1$ holds, the process is called thermal relaxation; if $(\Delta V/\Delta H)(C_p/V\theta) \gg 1$, it is called volume relaxation.

If the thermal relaxation is predominant, the relaxation frequencies depend strongly on temperature. However, as is shown in Tables II and III, the relaxation frequencies f_{r1} and f_{r2} are almost independent of temperature. Furthermore, the molecular structure of dextran leads us to the conclusion that the thermal relaxation due to the rotation of small segments hardly occurs. It is better to consider that the volume relaxation process is predominant in aqueous solutions of dextran.

From the literature, the hydration phenomenon was observed in aqueous solutions of dextran. One of the authors determined the amount of hydration as a function of temperature.[14] Gekko and Noguchi[15] investigated the molecular weight dependence of the amount of hydration, and they reported that the amount of hydration was independent of molecular weight for molecular weights higher than 2×10^3.

Considering these results, we may speculate that the acoustic wave perturbs the segmental motion of the

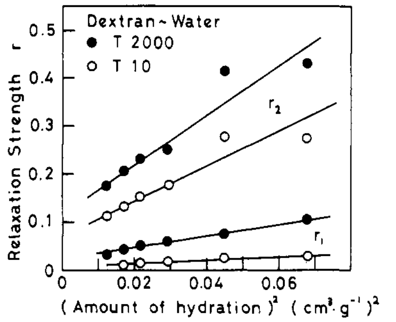

Figure 5. Relationship between relaxation strength, *r*, and amount of hydration: (●) dextran T-2000; (○) dextran T-10.

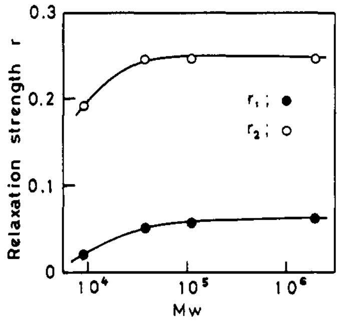

Figure 6. Relaxation strength, *r*, vs. molecular weight: (●) relaxation process 1 (low-frequency side); (○) relaxation process 2 (high-frequency side).

polymer chain in such a way as to cause rearrangement of water molecules weakly interacting with the polymer chain. This rearrangement gives rise to the volume relaxation.

In analogy with Ono et al.,[16] we can derive eq 3, which relates the ultrasonic relaxation strength *r* to the volume change ΔV in the segmental motion. ρ is the density, u

$$r \simeq \frac{2\mu_{\max}}{\pi} = \frac{\rho u^2}{M_s R T} C g H(x) (\Delta \bar{V})^2 \qquad (3)$$

is the sound velocity, M_s is the molecular weight of the segment, R and T are the ideal gas constant and absolute temperature, respectively, the function $H(x)$ is determined from the type of molecular motion, and g is the fraction of the segment associated with the motion in the polymer chain.

The $\rho u^2/T$ calculated from the experimental values of ρ and u is found to be almost independent of temperature. Assuming that $H(x)$ and M_s are independent of temperature yields the expectation of a linear correlation in the plots of r vs. $(\Delta V)^2$. We must also assume that ΔV can be substituted by the amount of hydration of dextran.

Figure 5 shows the relationship between the relaxation strength and square of the amount of hydration. Clearly, the linear correlation holds between them. Figure 6 shows the molecular weight dependence of relaxation strength. As is seen in Figure 6, the relaxation strengths are almost independent of molecular weight. This result is similar to that of hydration reported by Gekko and Noguchi.[15]

Thus, we have demonstrated that the ultrasonic relaxation processes observed in aqueous solutions of dextran are most likely associated with the exchange process of water molecules in the hydration sphere of the polymer.

References and Notes

(1) M. Wales, P. A. Marshall, and S. G. Weisberg, *J. Polym. Sci.*, **10**, 229-40 (1953).
(2) F. R. Senti, N. N. Hellman, N. H. Ludwig, G. E. Babcock, R. Tobin, C. A. Glass, and B. L. Lamberts, *J. Polym. Sci.*, **17**, 527-46 (1955).
(3) E. Antonini, L. Bellelli, M. R. Bruzzesi, A. Caputo, E. Chiancone, and A. Rossi-Fanelli, *Biopolymers*, **2**, 27-34 (1964).
(4) H. Nomura, S. Kato, and Y. Miyahara, *Mem. Fac. Eng. Nagoya Univ.*, **27**, 72-125 (1975).
(5) J. I. Dunber, A. M. North, R. A. Pethrick, and D. B. Steinhauer, *J. Polym. Sci.*, **15**, 263-77 (1977).
(6) S. A. Hawley and F. Dunn, *J. Chem. Phys.*, **50**, 3523-6 (1969).
(7) S. Kato, H. Nomura, and Y. Miyahara, *Polym. J.*, **11**, 455-61 (1979).
(8) W. J Gettins, P. L. Jobling, and E. Wyn-Jones, *J. Chem. Soc., Faraday Trans. 2*, 1246-52 (1978).
(9) D. A. MacIness and A. M. North, *Polymer*, **18**, 505-8 (1977).
(10) D. A. MacIness, *J. Polym. Sci.*, **15**, 657-74 (1974).
(11) D. Pugh and D. A. Jones, *Polymer*, **19**, 1008-14 (1978).
(12) W. H. Stockmayer and K. Matsuo, *Macromolecules*, **5**, 766-70 (1972).
(13) J. Lamb in "Physical Acoustics", Vol. II, Part A, W. P. Mason, Ed., Academic Press, New York, 1965, Chapter 4, pp 203-80.
(14) H. Nomura, S. Yamaguchi, and Y. Miyahara, *J. Appl. Polym. Sci.*, **8**, 2731-4 (1964).
(15) K. Gekko and H. Noguchi, *Biopolymers*, **10**, 1513-24 (1971).
(16) K. Ono, H. Shintani, O. Yano, and Y. Wada, *Polym. J.*, **5**, 164-75 (1973).
(17) W. Ludlow, E. Wyn-Jones, and J. Rassing, *Chem. Phys. Lett.*, **13**, 477-81 (1972).
(18) B. H. Zimm, *J. Chem. Phys.*, **24**, 269-78 (1956).

An Unusual Relaxation in Certain Copolymers of Ethylene and Propylene[†]

Howard W. Starkweather, Jr.

E. I. du Pont de Nemours and Co., Central Research and Development Department, Wilmington, Delaware 19898. *Received October 9, 1979*

ABSTRACT: In copolymers of ethylene and propylene made with vanadium-based catalysts and having relatively low E/P mole ratios, a secondary dynamic mechanical loss peak almost as large as that resulting from the glass transition was observed at −115 to −90 °C in experiments with a torsion pendulum. This phenomenon appears to be associated with dimethylene links and propylene reversals. The relaxation is not accompanied by a change in the coefficient of thermal expansion or the heat capacity and may be described in terms of a single relaxation time. It is seen in shear, but not in flexure. A similar polymer made with a titanium-based catalyst which does not contain reversed propylene units did not exhibit this relaxation.

Copolymers of ethylene and propylene constitute an important family of hydrocarbon elastomers. Terpolymers containing a diene monomer such as 1,4-hexadiene or ethylidenenorbornene as a cross-linking site are known as EPDM rubbers. A number of studies[1-6] have located the glass temperature, T_g, between −60 and −50 °C over a broad range of composition. There is a shallow minimum

---

[†] Contribution No. 2716.

0024-9297/80/2213-0892$01.00/0