

γ_ν changes slowly enough with ν for $(1 - \gamma_2/\gamma_\nu)$ to be virtually independent of ν . This assumption will lead to a lower limit for γ_∞ . Considering two paraffins with the number of carbon atoms ν_1 and ν_2 we then get for liquid polyethylene

$$\gamma_\infty = (\nu_1 - \nu_2)\gamma_{\nu_1}\gamma_{\nu_2}/[(\nu_1 - 2)\gamma_{\nu_2} - (\nu_2 - 2)\gamma_{\nu_1}] \quad (7)$$

and

$$v_\infty = v_{\text{CH}_2} = (\nu_1 + 1/7)v_{\nu_1} - (\nu_2 + 1/7)v_{\nu_2} \quad (8)$$

where the v 's are in units cubic centimeters per gram and the $1/7$ comes from changing the units from cubic centimeters per mole to cubic centimeters per gram.

Using Boelhouwer's data for *n*-nonane and *n*-hexadecane at the temperatures 30, 60, 90, and 120°, we get the points shown in Figure 3. These data have been fitted to an equation with the form

$$\gamma_\infty = A_0 + A_1v + A_2T + A_3vT \quad (9)$$

which yields

$$\gamma_\infty = (\partial S/\partial v)_T \text{ J/}^\circ\text{K cc} = 13.47 - 10.51v - 0.0303T + 0.0268vT \quad (10)$$

where v has the units cc/g and T the unit °C. (The standard deviation of the fit is 0.013 J/°K cc.)

One test of eq 10 is to compare it with the measured values at 140° and atmospheric pressure where the volume is 1.262 cc/g. The value computed from eq 10 is 0.69 J/°K cc, which compares well with the values of 0.68 J/°K cc quoted by Quinn and Mandelkern⁹ and 0.71 J/°K cc quoted by Starkweather and Boyd.¹⁰

(9) F. A. Quinn, Jr., and L. Mandelkern, *J. Amer. Chem. Soc.*, **80**, 3178 (1958).

(10) H. W. Starkweather, Jr., and R. H. Boyd, *J. Phys. Chem.*, **64**, 410 (1960).

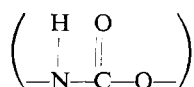
Low-Temperature Relaxations in Polyurethans

T. Kajiya and W. J. MacKnight

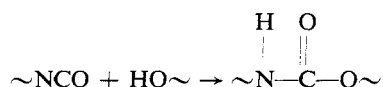
Department of Chemistry and Polymer Science and Engineering Program, University of Massachusetts, Amherst, Massachusetts 01002. Received December 2, 1968

ABSTRACT: A study has been made of the relaxation phenomena in three series of glassy polyurethans in the temperature range from -190 to -100° and at various frequencies up to 110 Hz using dynamic mechanical and dielectric relaxation. The structures of the repeat units of the three series are given in eq 1-3. Several overlapping relaxation peaks are discernible in the temperature and frequency region investigated. All of these relaxations arise largely from motion in the amorphous phase. The following assignments of the various relaxation peaks to specific molecular motions have been made on the basis of comparisons both within and among the three series. (1) The δ relaxation (-160°, 110 Hz) (4M series only) arises from hindered rotation of the methyl group attached to the 4 position of the benzene ring. (2) The γ_3 relaxation (-150°, 110 Hz) (H series only) arises from motions of methylene sequences in the diisocyanate part of the repeat unit. (3) The γ_2 relaxation (-140°, 110 Hz) arises from motions of methylene sequences, including oxygen, in the diol part of the repeat units of all three series. (4) The γ_1 relaxation (-120°, 110 Hz) arises from motions of methylene sequences including nonhydrogen bonded ester groups, and is active in all three series.

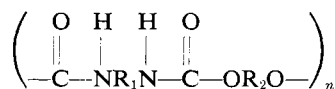
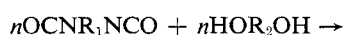
The term polyurethan refers to a large class of synthetic organic polymers having the common feature of containing the urethan linkage



The urethan linkage is not necessarily the only functional group present in the polymer nor is it necessarily the preponderant functional group. Polyurethans may be prepared by a variety of methods most of which involve the reaction of isocyanate (NCO) and hydroxyl (OH) groups to produce the urethan linkage according to



The polyurethans utilized in the present study were obtained by the step growth polymerization of a diisocyanate with a diol. Schematically



Three different diisocyanates were used, namely, 1,6-hexamethylene diisocyanate, 4,4'-diphenylmethane diisocyanate, and 4-methylmetaphenylene diisocyanate. The diols used ranged from 1,2-ethanediol to 1,10-decanediol. The structures of the repeat units of the polyurethans obtained by this procedure are given in eq 1-3. For convenience, in what follows the various series will be referred to as H-1,*n*, DP-1,*n*, and 4M-1,*n*, where *n* refers to the number of methylene units in the diol part of the repeat unit.

Polyurethans of the general structural type of the three series shown above have been investigated using the dynamic mechanical technique by several groups.¹⁻⁴ All of these polymers show three main relaxation regions and these are usually labeled α , β , and γ in order of decreasing temperature. It has been established that (1) the α relaxation is associated with the

(1) G. W. Becker and H. Oberst, *Kolloid Z.*, **152**, 1 (1957).

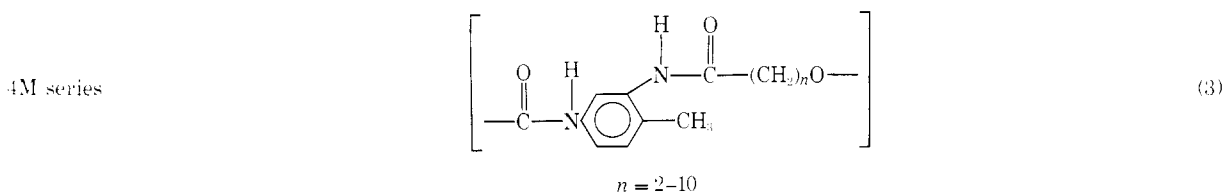
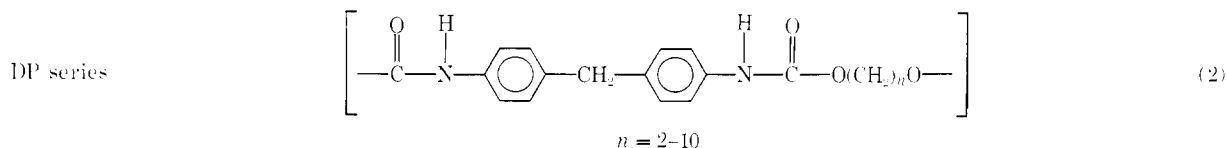
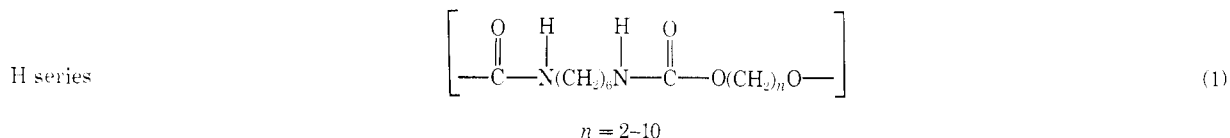
(2) K. H. Illers and H. Jacobs, *Makromol. Chem.*, **39**, 234 (1960).

(3) H. Jacobs and E. Jenckel, *ibid.*, **43**, 132 (1961); **47**, 72 (1961).

(4) For a review of the mechanical data on polyurethans through 1965, see N. G. McCrumb, B. E. Read, and G. Williams, "Anelastic and Dielectric Effects in Polymeric Solids," John Wiley & Sons, Inc., New York, N. Y., 1967, Chapter 12.

TABLE I

| Series | Polymerization temp, °C | Reaction time, hr |
|--------|-------------------------|-------------------|
| H | 115 | 18~26 |
| DP | 105 | 1.5-3 |
| 4M | 90 | 1.5-2 |

TABLE II
CARBON, HYDROGEN, AND NITROGEN ANALYSIS FOR THE VARIOUS SERIES OF POLYURETHANS

| Polymer | Calcd, % | | | Found, % | | |
|---------|----------|-------|-------|----------|-------|-------|
| | H | C | N | H | C | N |
| H 1,2 | 7.82 | 52.22 | 12.15 | 8.01 | 52.64 | 11.98 |
| H 1,5 | 8.26 | 57.42 | 10.31 | 8.44 | 56.87 | 10.02 |
| H 1,10 | 8.90 | 66.92 | 7.32 | 9.42 | 66.20 | 7.62 |
| DP 1,2 | 5.13 | 65.42 | 8.97 | 5.30 | 64.88 | 8.69 |
| 4M 1,2 | 4.50 | 54.00 | 12.62 | 5.84 | 52.31 | 9.9 |

main glass transition of the polymer, (2) the β relaxation is associated with water absorbed by the polymer, and (3) the γ relaxation has to do with local motions involving only a few main chain methylene units, probably including the polar groups. The details of the β and γ process in particular are not clear at the present time and it is the purpose of this paper to describe the γ relaxations of the H, DP, and 4M series and to propose specific molecular mechanisms for these relaxations. In order to accomplish this, recourse is had to the regular variation in structure within each series resulting from the differing methylene sequence lengths as well as to the variations in structure from one series to another.

Experimental Section

Materials and Polymerization Conditions. The starting diols and diisocyanates were obtained commercially. The diols from 1,2-ethanediol to 1,7-heptanediol and the three diisocyanates were purified by vacuum distillation. 1,8-Octanediol to 1,10-decanediol were purified by recrystallization from hexane.

The polymerization procedure followed the method of Lyman^{5,6} except that the polymerization temperatures and reaction times were modified as in Table I.

(5) D. J. Lyman, *Rev. Macromol. Chem.*, **1**, 191 (1966).

(6) "Macromolecular Synthesis," C. G. Overberger, Ed., John Wiley & Son, Inc., New York, N. Y., 1963.

An elemental analysis for carbon, hydrogen, and nitrogen was carried out and theoretical values for these elements were calculated on the assumption that the repeat units are exactly as depicted in the introduction and that no chain branching occurred due to allophanate formation or the presence of impurities. The results are given in Table II and it may be seen that the agreement is good. The deviations noted for hydrogen in the case of the 4M series probably arise from the presence of absorbed water, as this series is extremely hydrophilic.

Measurements. A. X-Ray. A continuous radial scanning technique was used with a molybdenum source. The degree of crystallinity was calculated from the ratio of the area of the crystalline peaks to the area of the amorphous peak. Only the H and DP series showed evidence of crystallinity by the X-ray method. In the case of the DP series it was possible to obtain completely amorphous material by quenching into a Dry Ice-alcohol mixture. In the H series, completely amorphous polymers were not obtainable in this way and so the measurement of the area of the amorphous peak had to be carried out by heating the polymers above their melting points.

B. Dynamic Mechanical Measurements. All measurements were carried out using a Vibron Dynamic viscoelastometer (Toyo Measuring Instrument Co.), Model DDV II. The temperature range was from -190 to -100° and the samples were heated at 1-2 deg/min under dry nitrogen. The frequencies of measurement were 3.5, 11, and 110 Hz.

C. Dielectric Relaxation. Measurements were carried out with a mutual inductance bridge, similar to the Cole-

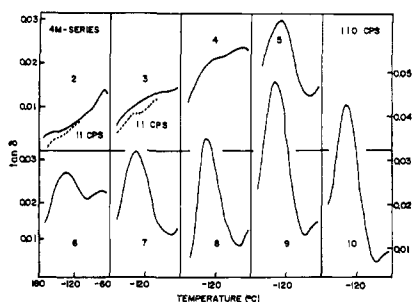


Figure 1. Temperature dependence of $\tan \delta$ at 110 Hz for the 4M series in the γ relaxation region.

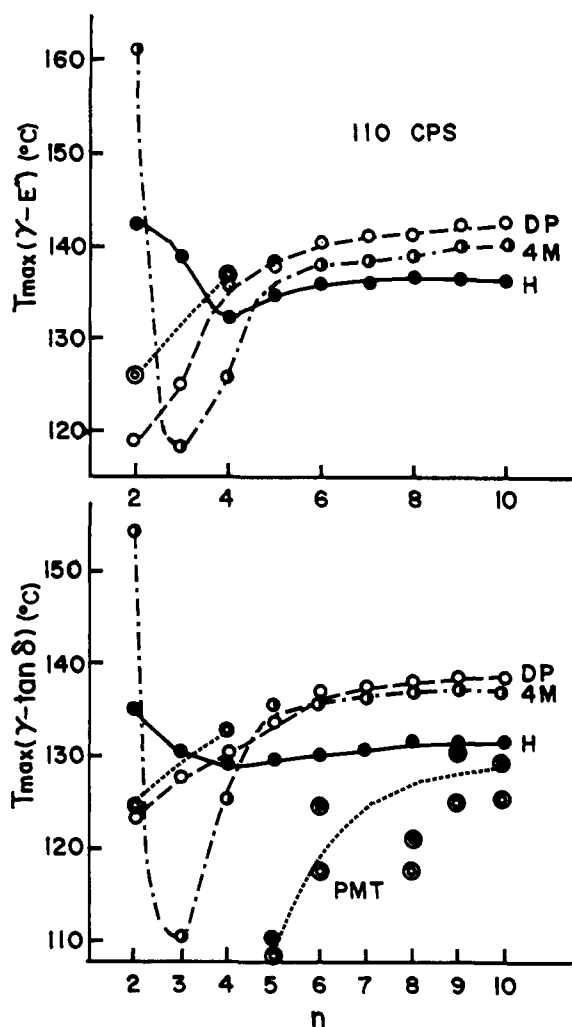


Figure 2. Dependence of the temperature of the γ peak maxima at 110 Hz on n , the number of CH_2 units in the diol part of the repeat units for E'' , $T_{\max}(\gamma - E'')$, and $\tan \delta$, $T_{\max}(\gamma - \tan \delta)$. Also included are corresponding temperatures of peak maxima for poly ethers and poly(methylene terephthalates) (PMT, \odot). All temperatures listed on the ordinate should be negative values.

Gross bridge. The apparatus was constructed with three terminal electrodes in order to avoid edge and surface effects as well as the stray capacity effect. Samples were sputtered with silver on both surfaces and were kept sealed under dry nitrogen to avoid absorption of water. The temperature range used was from -190 to -20° and all measurements were carried out at 100 Hz.

Sample Preparation. 1. The H and DP series samples

were compression molded into films suitable for mechanical testing at 10° above their melting points. The films were allowed to cool in air to room temperature or they were quenched to various temperatures by plunging them into liquid nitrogen.

2. The 4M series samples were compression molded into films at temperatures approximately 50° in excess of their T_g 's.

3. Annealing was carried out in an oil bath with the samples enclosed in a sealed tube under dry nitrogen.

Results

The temperature region investigated encompasses the so-called γ -relaxation region for all three series of polyurethans. Figure 1 gives the temperature dependence of the mechanical loss tangent, $\tan \delta$, for the 4M series. It is seen that for 4M-1,2 and -1,3, there is a small, very low temperature relaxation peak (to be discussed later), but the main γ peak is absent at 110 Hz. There is some evidence for a small γ peak in 4M-1,3 at 11 Hz. It is at once apparent from inspection of Figure 1 that the magnitude and temperature location of the γ relaxation is sensitive to n , the number of methylene units in the diol part of the repeat unit. This behavior is general for all three series and forms the basis for the molecular interpretation of the γ relaxation in the polyurethans investigated.

Figure 2 shows the dependence of the temperature of the γ peak maximum on n . The temperatures of the E'' and $\tan \delta$ maxima are both plotted and both show the same trends. With the exception of 4M-1,2, both the 4M and DP series show the same behavior which is a gradual decrease in peak temperature as n increases. 4M-1,2 displays a peak with a maximum at the anomalously low value of -160° , much lower than that observed for any of the other polymers in any series. The H series exhibits a small increase in temperature in going from H-1,2 to H-1,4 and then the same general trend as the DP and 4M series for the higher values of n . For the sake of comparison are also plotted temperatures of the peak maxima for the poly ethers,⁷ poly(ethylene oxide), $[-\text{OCH}_2\text{CH}_2\text{O}-]_n$, and poly(tetramethylene oxide),⁷ $[-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-]_n$, as well as the temperatures of the peak maxima of a series of poly(methylene terephthalates),⁸ $[-p\text{-COC}_6\text{H}_4\text{O}(\text{CH}_2)_x\text{O}]_n$ for $x = 5-10$. The comparisons are somewhat suspect in that the frequencies at which the measurements on these polymers were made were somewhat different from those used in the present work. However, the assumption was made that the γ peak had an activation energy comparable to that observed for the polyurethans and the peak temperatures were thus adjusted to 110 Hz on this basis. It can be seen that the poly ether data corresponds quite closely to the DP and 4M series while the polymethylene terephthalates show peak temperatures higher than those observed in the polyurethans. The polymethylene terephthalates show tendencies for the peak temperatures to decrease with increasing n in a similar manner to the behavior of the DP, H, and 4M series.

The activation energies of the γ process for the three series are plotted as a function of n in Figure 3. (These

(7) M. Takayanagi, K. Imada, and T. Kajiyama, *J. Polym. Sci., Part C*, **15**, 263 (1966).

(8) I. M. Ward, *J. Macromol. Sci.*, **B1** (4), 667 (1967).

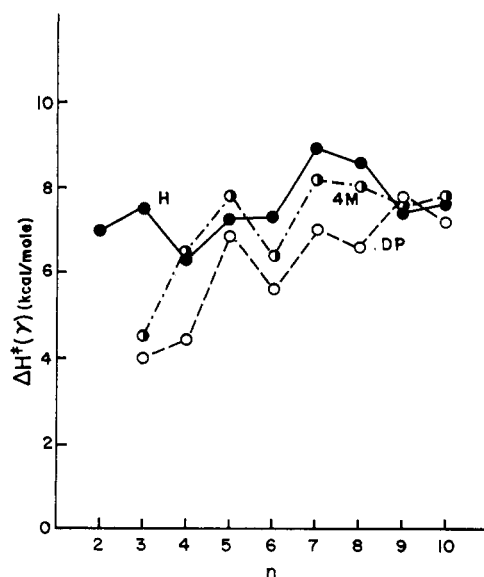


Figure 3. The activation energy of the γ relaxation ($\Delta H^\ddagger(\gamma)$) as a function of n , the number of CH_2 units in the diol part of the repeat units for all three series.

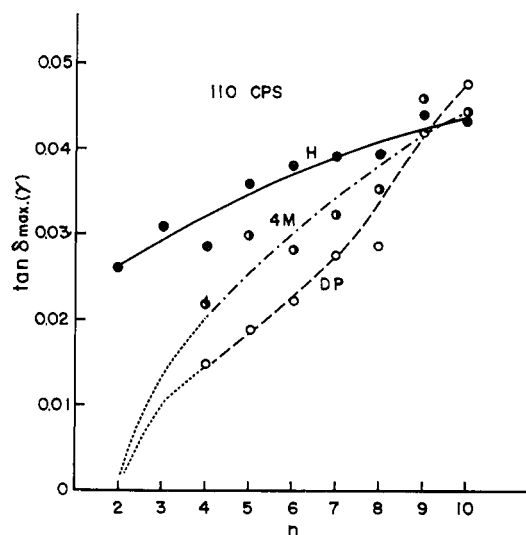


Figure 4. Maximum intensity of the $\tan \delta$ peak of the γ relaxation at 110 Hz as a function of n , the number of CH_2 units in the diol part of the repeat units for all three series.

values are obtained in the normal manner, *i.e.*, from the slope of the line resulting from a plot of the logarithm of frequency *vs.* the reciprocal of the absolute temperature of the peak maximum at the corresponding frequency.) Although the points are somewhat scattered, it can be seen that the activation energy shows a general increase with increasing n for the DP and 4M series. There is no apparent regular trend in the case of the H series. As a basis for comparison may be cited the dielectric studies of Michailov,⁹ who investigated the activation energy of the γ process for a series of poly(n -alkyl acrylates) of varying side chain lengths. It was found that the activation energy remained constant at a value of 9 kcal mol⁻¹, inde-

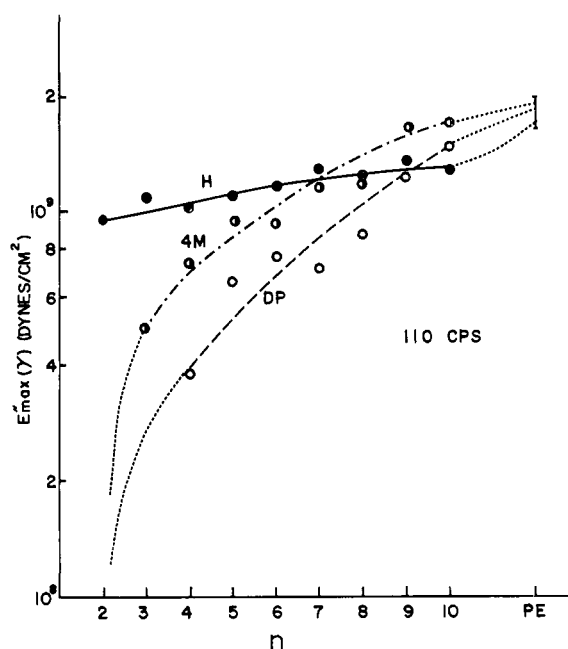


Figure 5. Maximum intensity of the E'' peak of the γ relaxation at 110 Hz as a function of n , the number of CH_2 units in the diol part of the repeat units for all three series.

pendent of the length of the side chain. The γ process in the polyacrylates is thought to arise from local motions of three or more methylene units in the side chain. It would thus appear that the main chain γ process in the polyurethans differs in its mechanism from the side chain relaxation in the poly(alkyl acrylates).

Figures 4 and 5 show the dependence of the magnitude of the $\tan \delta$ peaks and the E'' peaks on n for the various series at 110 Hz. The γ peak is essentially absent for values of n less than 4 at 110 Hz for both the DP and 4M series, while it is present for all values of n in the case of the H series. (For the moment, the peak occurring at -160° for 4M-1,2 and 4M-1,3 is not included in the discussion.) In all series, the magnitude of the peaks show a tendency to increase with increasing n , although this is much less marked in the H series than in the 4M and DP series.

The Effect of Thermal History on the γ Relaxation.

Figures 6 and 7 show the temperature dependence of $\tan \delta$ and E'' in the γ region for H-1,2 and H-1,5, respectively, as well as the effect of various thermal treatments on the shapes of these peaks. It can be seen from Figures 6 and 7 that the γ relaxation for the H series consists of three different overlapping peaks. These are labeled γ_1 , γ_2 , and γ_3 in order of decreasing temperature and are most clearly evident in the case of the E'' plots for the annealed samples. Figure 8 shows the behavior of DP-1,5 under the same conditions, and it can be seen that there now appear to be only two overlapping peaks, labeled γ_1 and γ_2 in the figure. In this case the two peaks are most clearly evident in the quenched $\tan \delta$ plot. The 4M series behaves in a similar manner to the DP series as shown in Figure 9, except that, for 4M-1,5, which is chosen for purposes of illustration, the two overlapping peaks are best distinguished in the annealed E'' plot.

(9) G. P. Michailov and T. I. Bousev, *Polym. Sci. USSR*, **6**, 1971, 1979 (1964).

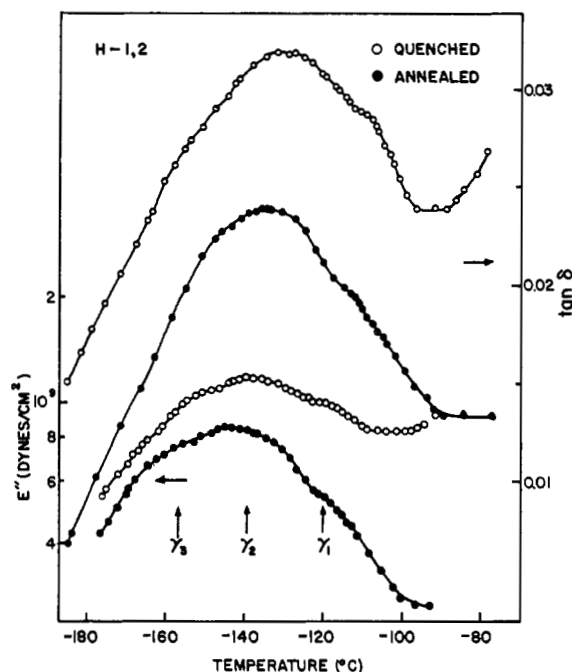


Figure 6. Temperature dependence of $\tan \delta$ and E'' in the γ region at 110 Hz for H-1,2 subjected to the thermal treatments indicated in the figure.

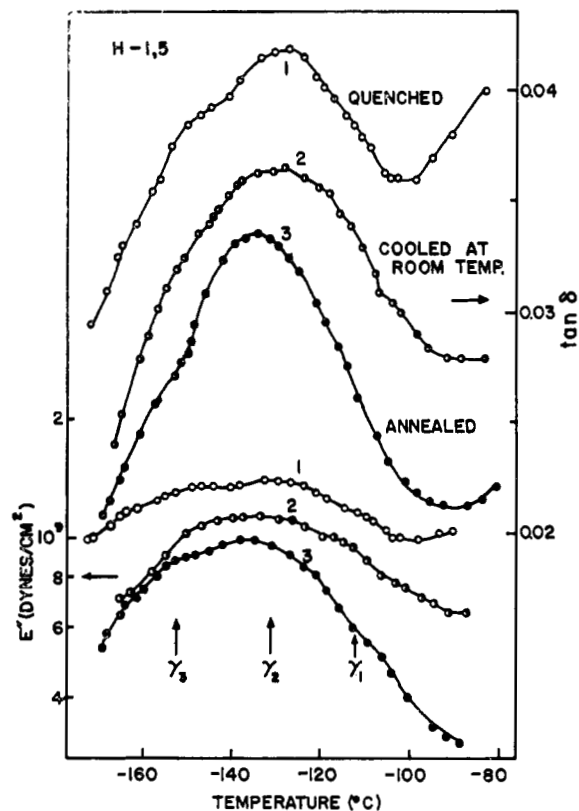


Figure 7. Temperature dependence of $\tan \delta$ and E'' in the γ region for 110 Hz for H-1,5 subjected to the thermal treatments indicated in the figure.

As a general rule, inspection of Figures 6–9 reveals that the over-all magnitude of the γ relaxation peak is decreased by annealing. Also, the γ_1 process becomes relatively less prominent on annealing. Annealing has two effects: it increases the degree of crystallinity

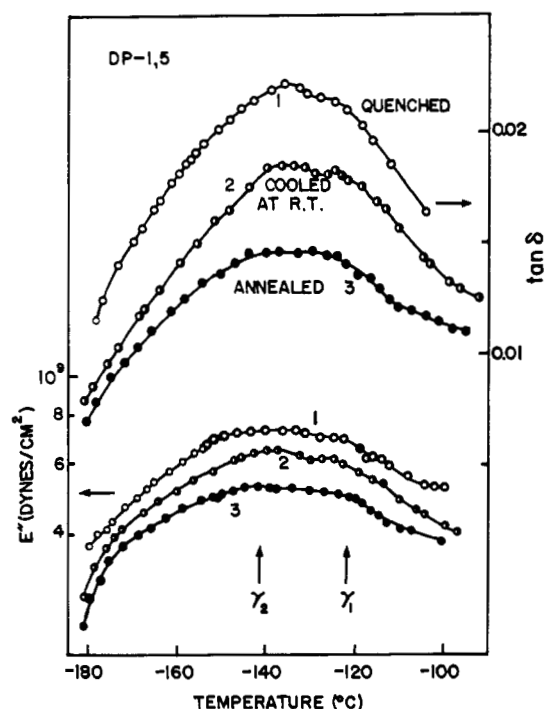


Figure 8. Temperature dependence of $\tan \delta$ and E'' in the γ region at 110 Hz for DP-1,5 subjected to the thermal treatments indicated in the figure.

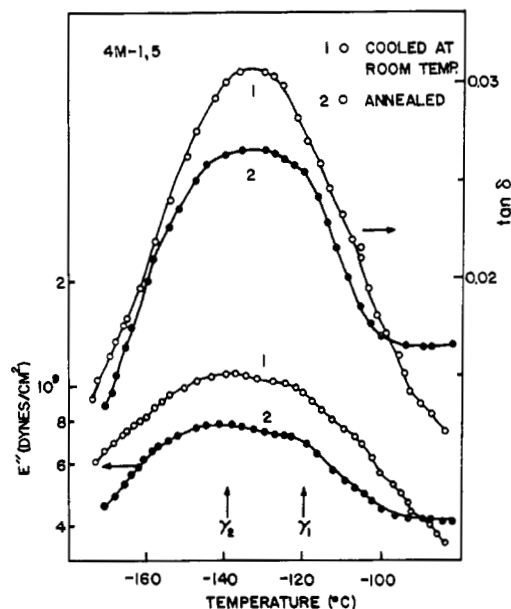


Figure 9. Temperature dependence of $\tan \delta$ and E'' in the γ region at 110 Hz for 4M-1,5 subjected to the thermal treatments indicated in the figure.

as measured by the X-ray method in the case of the H and DP series, and it increases the amount of hydrogen bonding for all three series. (The 4M series remains completely amorphous as determined by X-rays regardless of the thermal history.) The decrease in the magnitude of the over-all γ process with annealing is thus indicative of an amorphous phase origin for the process and/or an association with hydrogen bonded groups.

The δ Relaxation. Figure 10 shows the temperature dependence of E'' in the region of -180 to -100°

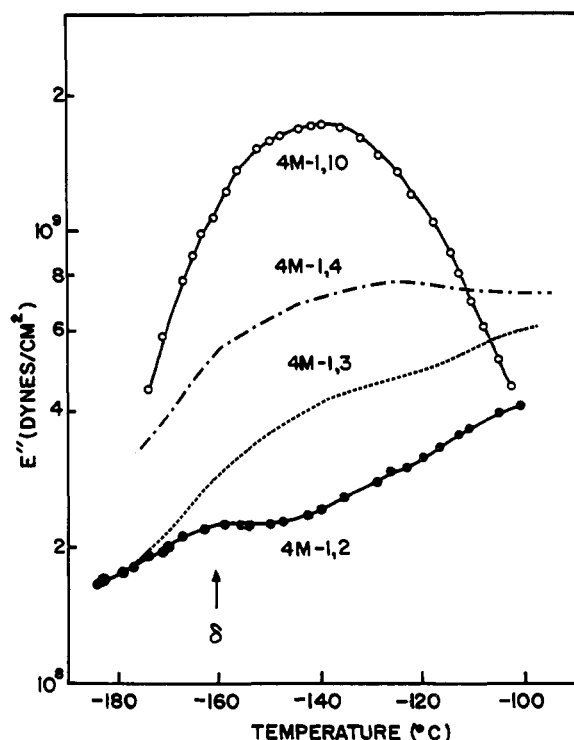


Figure 10. Temperature dependence of E'' at 110 Hz for various members of the 4M series showing the δ relaxation.

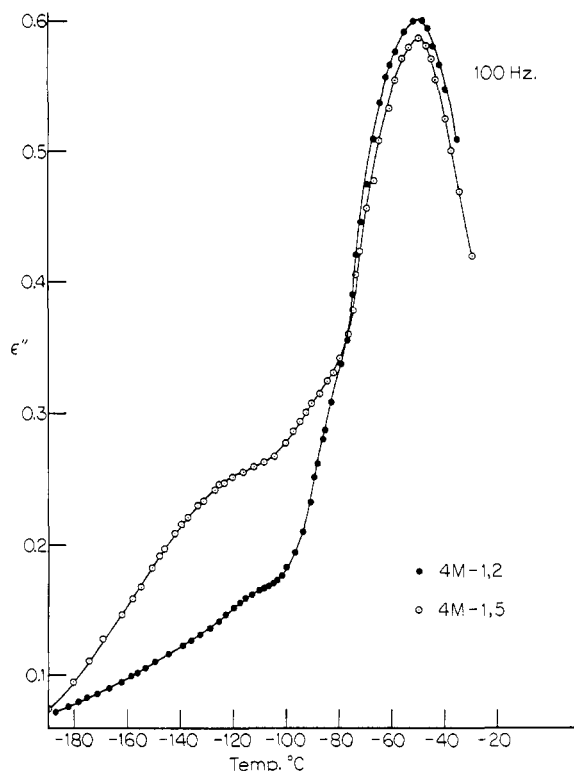


Figure 11. Temperature dependence of ϵ'' at 100 Hz for 4M-1,2 and 4M-1,5 in the γ relaxation region.

for several members of the 4M series. It is readily seen that 4M-1,2 does not exhibit any well-defined peak in the γ region of -140 to -120° . Rather, a small peak with a maximum at -160° is noted. This is labeled δ and is seen to persist for the higher members of the 4M series in the form of a shoulder on the γ relaxation

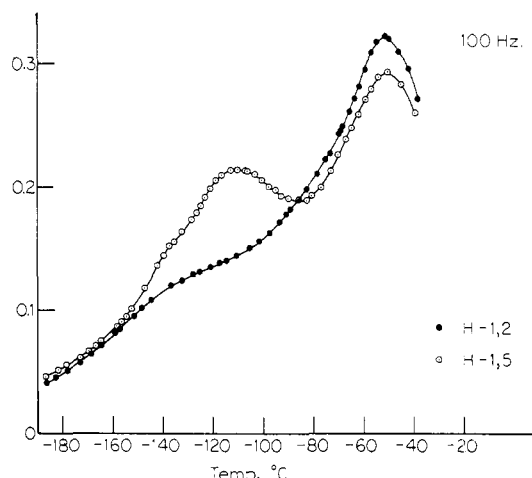


Figure 12. Temperature dependence of ϵ'' at 100 Hz for H-1,2 and H-1,5 in the γ relaxation region.

peak. The anomalous temperature of the peak maximum of the δ peak relative to the "normal" γ peak temperature of the other members of the 4M series has already been noted, as well as the absence of this peak in the DP and H series. It is thus proposed that the δ relaxation arises from a separate and distinct molecular mechanism that is different from the γ relaxations observed for all three series.

The Dielectric γ Relaxation. Figures 11 and 12 show the temperature dependence of the dielectric loss, ϵ'' , for two members of the 4M series and two members of the H series, respectively. The higher temperature peak located in the -40 to -60° range is apparently connected with absorbed water and is the subject of a subsequent publication. It will not be discussed further at this time except to note the fact that this peak overlaps the dielectric γ relaxation quite severely in all three series. In the case of the 4M series, Figure 11 shows that the dielectric γ relaxation behaves in a similar manner to the mechanical γ relaxation insofar as an increase in magnitude occurs with increasing n . However, the dielectric γ relaxation is not completely absent for 4M-1,2 as it is in the mechanical case, but rather a small peak is discernible at -110° , although precise location is difficult because of the overlap of the water peak. In contrast to the mechanical results, the dielectric data show no trace of the δ relaxation peak. Turning to the H series, Figure 12 shows that the dielectric γ relaxation for H-1,2 is much smaller in magnitude than the mechanical γ relaxation for the same polymer. H-1,5 exhibits an asymmetric dielectric γ peak which appears to consist of two overlapping peaks in contrast to the three overlapping peaks of the mechanical γ relaxation.

Discussion

In light of the results presented above it is possible to propose molecular mechanisms responsible for the loss peaks observed in the low-temperature region. Each relaxation will be discussed in turn starting at the low-temperature end.

The δ Relaxation. It has already been suggested in the results section that the δ relaxation arises from a mechanism distinct from that of the γ relaxation.

Inasmuch as this relaxation occurs only in the 4M series it is reasonable to suspect it to be associated with a structural feature occurring in the 4M series but absent in the DP and H series. The 4M series possesses the unique structural characteristic of having a methyl group attached to the 4 position of the benzene ring (see the structure of the repeat unit given in the beginning of this article). In the case of poly(methyl methacrylate), a loss peak assigned to the rotation of the α methyl group has been observed by mechanical measurements^{10,11} and by nmr line width studies.¹² This loss peak occurs at a temperature of -173° at 1 Hz. Allowing for the frequency difference of the measurement, this value is quite close to the temperature of the δ relaxation observed in the present work. It thus seems reasonable to assign the δ relaxation to the rotation of the methyl group attached to the 4 position of the benzene ring.

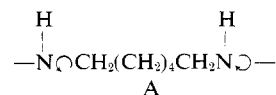
It has been pointed out¹³ that the rotation of a methyl group cannot give rise to mechanical loss if the potential energy as a function of rotation angle is given by three energetically equivalent minima each separated by 120° as has generally been supposed. It thus appears that the potential energy must be some more complex function of the rotation angle of the methyl group than would be expected on the basis of the simple rotational isomer model. In the case of the 4M series it seems reasonable to expect this behavior in view of the possibility of interaction of the methyl group with both the benzene ring and the neighboring polar urethan linkage.

The absence of a dielectric δ relaxation also lends support to the assignment of the mechanical δ relaxation to methyl group rotations. Since such motions do not involve any dipole reorientations, they would not be expected to give rise to a dielectric loss peak.

The γ Relaxation. Since the γ relaxation in the polyamides has been extensively investigated, the findings will be used as a basis for the discussion of the γ relaxation in the polyurethans studied here. The polyamides differ structurally from the polyurethans only in that the -NHC(=O)O- group in the polyurethans is replaced by the -NHC(=O)- group in the polyamides. The following facts have been established concerning the γ relaxation in the polyamides.¹⁴ (1) The γ relaxation in polyamides arises in part from the motion of $(\text{CH}_2)_n$ units between amide groups, with $n \geq 3$. (2) The polar amide groups are partially responsible for the γ relaxation. (3) The activation energy of the γ relaxation is 9–10 kcal mol⁻¹.

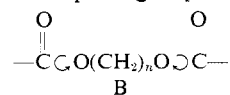
Low-temperature relaxations of the γ type have been observed for a great many polymers of different structural characteristics. It has been proposed, notably by Schatzki,¹⁵ that the mechanism of the γ relaxation consists of the hindered rotation of a few methylene groups as a unit. These groups may be located either in the main chain or in side chains. The essential features of the model of Schatzki are that the end bonds

of the rotating unit of methylene sequences are colinear and remain fixed. In order for this condition to be met, assuming tetrahedral bond valence angles, equal bond lengths and the rotational isomer conformation model, it must be that in the sequence $\text{-CH}_2\text{-CH}_2\text{-(CH}_2)_n\text{-CH}_2\text{-CH}_2\text{-}$, $n = 4$ or greater. Parenthetically, it should be noted that such a mechanism must be operative in the amorphous phase since, in the crystal phase, all the CH_2 groups are in the *trans* conformation (0° rotational angle) and this does not allow for the colinearity of the end bonds required by Schatzki's mechanism. However, it has been shown, at least for the cases of polyethylene,¹⁶ an ethylene-methacrylic acid copolymer,¹⁷ and polychlorotrifluoroethylene,¹⁸ that the γ transition arises partially from the crystalline phase. Thus a crystalline contribution to the γ relaxation in the case of the polyurethans cannot be entirely ruled out. Restricting attention to the amorphous phase for the moment, and adopting Schatzki types of mechanisms for the γ relaxation in the polyurethans, the following sequential structures (A–C) may be examined in addition to methylene sequences alone.



Here the N–C bonds act as the rotation axis for the methylene sequence and it is presumed that the NH groups are fixed by intermolecular hydrogen bonds. This case is thus really identical with the Schatzki model and would be expected to be active in the H series only. Inasmuch as the γ_3 relaxation occurs only in the H series, it may reasonably be assigned to the above type of motion.

The strict application of the above mechanism to the γ_3 process would indicate the absence of a dielectric γ_3 peak since, as in the δ process, no dipole reorientation is involved. As will be discussed shortly, the conclusion may also be reached that no dielectric γ relaxation of any kind should be present for H-1,2. While it is true that the dielectric γ relaxation in H-1,2 is much smaller in magnitude than the mechanical γ relaxation in H-1,2, Figure 12 nevertheless reveals traces of a γ peak. A plausible explanation for this is that the γ_3 process causes a certain amount of motion of the polar groups to take place. This need not involve rotations but may only consist of vibrations or torsional oscillations. The requirement of dipole reorientation would obviously be satisfied by many types of motion of the polar groups.



In this case, which is common to all three series, the carbonyl groups are considered fixed once again by intermolecular hydrogen bonds and the C–O bonds define the rotation axis. If we enforce the condition of colinearity of the C–O bonds, then rotation of

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(13) See ref 4, p 248.

(14) See ref 4, p 496.

(15) T. F. Schatzki, *J. Polym. Sci.*, **57**, 496 (1962).

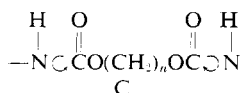
(16) S. Matsuoka, Y. Ishida, and C. J. Aloisio, presented at IUPAC International Symposium on Macromolecular Chemistry, Tokyo, Japan, Sept 1966.

(17) L. W. McKenna, T. Kajiyama, and W. J. MacKnight, *Macromolecules*, in press.

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the methylene groups and oxygens as a unit can occur for $n \geq 4$. The essential absence of a γ peak in the DP and 4M series for the polymers containing two or three methylene units in the diol part is in accord with the proposal that n must be 4 or greater. In addition the good agreement between the temperatures of the low-temperature relaxation in the poly ethers and the γ relaxation of the 4M and DP series indicates identical molecular mechanisms in the two cases.

It has been shown by Wetton and Williams¹⁹ that the low-temperature dielectric loss peak in poly(tetramethylene oxide) is located at a comparable position to the low-temperature mechanical loss peak of this polymer, namely, -110° at 100 Hz. (It should be pointed out that the best comparison between dielectric and mechanical results is obtained using the mechanical $\tan \delta$ and the dielectric ϵ'' .) It can be seen from Figures 11 and 12 that the main dielectric γ peak for both the 4M and H series is also located in this vicinity. It would thus appear that the main dielectric γ peak in the polyurethans is identical with the γ_2 mechanical relaxation in the polyurethans and arises from the same molecular mechanism responsible for the low-temperature dielectric and mechanical loss peaks in poly(tetramethylene oxide), that is, motions of type B. Figure 12 shows that there is a small shoulder on the low-temperature side of the main dielectric γ loss peak in H-1,5. Inasmuch as this occurs at approximately the same temperature as the γ relaxation in H-1,2, it seems reasonable to assume that this peak is the result of motions of the polar groups induced by the γ_3 mechanism. The presence of but a single γ peak between -180 and -110° in 4M-1,5 (Figure 11) also tends to confirm this assignment.



This case is again common to all three series and it is assumed that the N-H groups are fixed by hydrogen bonding, but the C=O groups are not hydrogen bonded. Once again, enforcing the colinearity of the N-C bonds, rotation of the unit composed of the methylene groups and the ester groups can occur if $n \geq 5$. There are two major pieces of evidence indicating that motions of type C are responsible for the γ_1 relaxation. The first is that annealing, which is known to increase the degree of hydrogen bonding, decreases the magnitude of the γ_1 relaxation relatively more than either the γ_2 or γ_3 relaxation. The second is that the low temperature relaxation in poly esters, which may reasonably be assumed to arise from type C motions, occurs at a slightly higher temperature than the low temperature relaxations in polyethylene and the poly ethers. (See Results.) Type C motions should obviously be dielectrically active. However, the overlap of the very strong dielectric water peak prevents the γ_1 dielectric relaxation from being resolved. Resolution might be obtained at lower frequencies and experiments are currently underway to investigate this point.

In both cases B and C we have mentioned free rota-

tion of the units as a whole. In fact, this is an extreme situation and both the γ_2 and γ_1 relaxation probably involve only torsional oscillations rather than free rotation. This may be especially true of the γ_1 relaxation since the proposed mechanism involves motions about the N-C bond. It is known that similar N-C bonds in polyamides and polypeptides possess considerable double bond character²⁰ and, assuming this to be true of the polyurethans also, it seems doubtful that free rotation about the N-C bonds would occur at low temperatures.

The mechanisms proposed here for the γ relaxation require that there be no mechanical γ relaxation peak for 4M-1,2, 4M-1,3, DP-1,2, and DP-1,3, and this is borne out by the experimental facts. However, H-1,2 should show a single γ relaxation peak which would be identified as γ_3 and should be dielectrically inactive. Figure 6 shows the presence of all three mechanical γ peaks in H-1,2 and the presence of a small dielectric γ peak has already been commented on. The probable explanation for this behavior is that the γ_3 type motion, the motion of six CH_2 sequences, induces the motion of the polar groups and thus causes both dielectric activity and the presence of a mechanical γ_2 and γ_1 in H-1,2.

The question of a partial crystalline origin for the γ relaxation in the polyurethans cannot be settled at the present time. It is certain that the γ relaxation in the polyurethans arises largely in the amorphous phase as shown by its presence in the 4M series and by the decrease in magnitude observed on annealing. It is realized that the mechanisms proposed here are but first approximations to the true behavior but it is hoped that they will serve as a basis for further refinements concerning the elucidation of low-temperature relaxations in polar polymers.

Conclusions

The low-temperature relaxations in the polyurethans investigated in this study consist of several overlapping peaks which arise largely from motions in the amorphous phase.

The δ relaxation (-160° , 110 Hz) is due to rotation of the methyl group attached to the four position of the benzene ring in the diisocyanate part of the repeat unit of the 4M series.

The γ_3 relaxation (-150° , 110 Hz) arises from motions of methylene sequences in the diisocyanate part of the repeat unit of the H series.

The γ_2 relaxation (-140° , 110 Hz) arises from motions of methylene sequences including oxygen in the diol part of the repeat unit of all three series.

The γ_1 relaxation (-120° , 110 Hz) arises from motions of methylene sequences including ester groups with nonhydrogen bonded carbonyl groups in all three series.

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(20) We are grateful to the reviewer for pointing out the possible double bond character of the N-C bond.