pension structures,[24-28] the conformation of flexible polyelectrolytes,[29-31] and dynamic properties of macroions.[32,33]

Figure 5 shows the concentration dependencies of the rotational relaxation times of HPAA. The τ_r's decreased slightly (especially for HPAA of $\alpha = 0.177$) as the polymer concentration increased. This means that the conformation of HPAA begins to shrink with increasing concentration, which is reasonable if we take into account the increased effect of electrostatic shielding on the intramacroion repulsion with polymer concentration.

It should be emphasized here that the relaxation times observed by the CSF method do not always give only the fast rotational relaxation times (τ_r). The slower relaxations, which are usually over 10 times larger, are often observed, especially for low molecular weight HPAA samples. The slow process is identified tentatively as the fluctuation of local assemblies of macroions in solution. Regrettably, the values of relaxation times reported previously for HPAA solution[13] were slow steps, not the fast rotational ones, because the previous relaxation time data were too large compared with those expected from the theory, eq 3.

In conclusion, the rotational relaxation times of poly(acrylic acid) are observed by the conductance stopped-flow technique. The conformation of the macroion is found to be highly stretched at high degrees of neutralization (α). The chain shrinks with decreasing α. The highly deionized HPAA molecules at $\alpha = 0$ are stretched.

Registry No. HPAA, 9003-01-4.

References and Notes

(1) Okubo, T. *J. Am. Chem. Soc.* **1987**, *109*, 1913.
(2) Okubo, T. *J. Phys. Chem.* **1987**, *91*, 1977.
(3) Okubo, T. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 703.
(4) Heckmann, K. *Z. Phys. Chem., N.F.* **1959**, *9*, 318.
(5) Gotz, K. G.; Heckmann, K. *J. Colloid Sci.* **1958**, *13*, 266.
(6) Schindewolf, U. *Z. Elektrochem.* **1954**, *58*, 697.
(7) Eigen, M.; Schwarz, G. *J. Colloid Sci.* **1957**, *12*, 181.
(8) Schwarz, G. *Z. Phys. Chem., N.F.* **1959**, *19*, 286.
(9) Heckmann, K.; Gotz, K. G. *Z. Elektrochem.* **1958**, *62*, 281.
(10) Gotz, K. G. *J. Colloid Sci.* **1965**, *20*, 289.
(11) Kern, E. E.; Anderson, D. K. *J. Polym. Sci., A1* **1968**, *6*, 2765.
(12) Okubo, T.; Kitano, H.; Ishiwatari, T.; Ise, N. *Proc. R. Soc. London, Ser. A* **1979**, *366*, 81.
(13) Okubo, T. *Biophys. Chem.* **1980**, *111*, 425.
(14) Okubo, T.; Enokida, A. *J. Chem. Soc., Faraday Trans. 1* **1983**, *79*, 1639.
(15) Okubo, T.; Hongyo, K.; Enokida, A. *J. Chem. Soc., Faraday Trans. 1* **1984**, *79*, 1639.
(16) Kitano, H.; Hasegawa, J.; Iwai, S.; Okubo, T. *Polym. Bull.* **1986**, *16*, 89.
(17) Kitano, H.; Hasegawa, J.; Iwai, S.; Okubo, T. *J. Phys. Chem.* **1986**, *90*, 6281.
(18) Sawamoto, M.; Higashimura, T.; Enokida, A.; Okubo, T. *Polym. Bull.* **1980**, *2*, 309.
(19) Okubo, T. *Dynamic Aspects of Polyelectrolytes and Biomembranes*; Oosawa, F., Ed.; Kodansha: Tokyo, 1982; p 111.
(20) Okubo, T. *Makromol. Chem. Suppl.* **1985**, *14*, 161.
(21) Heckmann, K. *Naturwissenschaften* **1953**, *40*, 478.
(22) Jacobson, B. *Rev. Sci. Instrum.* **1953**, *24*, 949.
(23) Schwarz, G. *Z. Phys.* **1956**, *145*, 563.
(24) Hachisu, S.; Kobayashi, Y .; Kose, A. *J. Colloid Interface Sci.* **1973**, *42*, 342.
(25) Pieranski, P. *Contemp. Phys.* **1983**, *24*, 25.
(26) Okubo, T. *J. Chem. Soc., Faraday Trans. 1*, **1986**, *82*, 3185.
(27) Okubo, T. *J. Chem. Phys.* **1987**, *86*, 2394, 5182.
(28) Okubo, T. *J. Chem. Phys.* **1988**, *88*, 2083.
(29) Barenes, C. J.; Chan, D. Y.; Everett, D. H.; Yates, D. E. *J. Chem. Soc., Faraday Trans. 1*, **1978**, *74*, 136.
(30) Giordano, R.; Maisano, G.; Mallamace, F.; Micali, N.; Wanderlingh, F. *J. Chem. Phys.* **1984**, *88*, 5368.
(31) Drifford, M.; Dalbiez, R. H. *J. Phys. Chem.* **1984**, *88*, 5368.
(32) Shaw, J. N.; Ottewill, R. H. *Nature (London)* **1984**, *208*, 681.
(33) Goff, J. R.; Luner, P. *J. Colloid Interface Sci.* **1984**, *99*, 468.

Dielectric and Mechanical Relaxations in Cycloaliphatic Polyformal Networks

Ricardo Díaz-Calleja, Amparo Ribes, and José L. Gómez

Laboratorio de Termodinámica y Físico-Química, ETSIIV, UPV, Valencia, Spain

Evaristo Riande* and Julio Guzmán

Instituto de Ciencia y Tecnología de Polímeros (CSIC), 28006-Madrid, Spain.

Received May 4, 1988; Revised Manuscript Received September 30, 1988

ABSTRACT: Poly(*cis/trans*-1,4-cyclohexanedimethanol-*alt*-formaldehyde) (PCDO) chains, obtained by condensation of the cis, cis/trans (28/72), and cis/trans (10/90) isomers of 1,4-cyclohexanedimethanol with formaldehyde, were cross-linked with an aromtic triisocyanate. The networks exhibit a well-developed α process associated to the glass–rubber transition, whose location is relatively independent of the substitution (eq–ax or eq–eq) of the cyclohexane ring. The cis isomer presents a mechanical subglass absorption, labeled β, centered at −60 °C at 1 Hz and a weak γ relaxation. The fact that a similar β process also appears at the same temperature and frequency in poly(*cis*-1,4-cyclohexanedimethanol sebacate) (*cis*-PCDS) suggests that the relaxation is caused by molecular motions associated to the glycol residue. The dielectric relaxation spectra exhibit, in addition to the glass–rubber relaxation, two subglass peaks whose maxima are located at −30 (β) and −74 °C (γ), at 0.5 kHz. Since the activation energy of the dielectric β peak is 18.1 kcal mol^{-1}, the absorption would be centered at ca. −65 °C, at 1 Hz, almost at the same temperature as the mechanical one, suggesting that similar molecular motions produce both relaxations. The mechanical subglass region in the relaxation spectra of *cis/trans*(10/90)-PCDO networks resembles that of poly(*trans*-1,4-cyclohexanedimethanol sebacate) (*trans*-PCDS) in that a broad and diffuse relaxation, extending in a temperature span of more than 100 °C, appears. An inspection of this region in the *cis/trans*(28/72)-PCDO networks indicates that complex molecular motions involving more than a single structural unit are responsible for the mechanical β relaxation. Two peaks centered at −30 (β_1) and −60 °C (β_2) are detected in the subglass dielectric relaxation of the networks with the highest *trans*-cyclohexylene units content. Finally, the free volume interpretation gives a good account of the mechanical and dielectric relaxation processes that take place in the glass–rubber transition.

Introduction

The study of the secondary relaxations in polymers containing six-membered saturated rings bonded to the chains has been the subject of numerous investigations in the past.[1-9] As far as the subglass relaxations are concerned, polymers with cyclohexyl rings anchored to side groups show a prominent relaxation process at a frequency around 1 Hz at temperatures in the vicinity of −80 °C,

0024-9297/89/2222-1821$01.50/0

whose activation energy[5] amounts to 11–12 kcal mol^{-1}. The absorption also appears on dynamic mechanical curves of polymers plasticized by low molecular weight compounds containing a cyclohexane ring. The fact that the value of the activation energy of the process is similar to that involved in the chair-to-chair transition in cyclohexane rings suggests that the prominent subglass absorption is caused by flipping motions of the cyclohexyl group.[5] However, this behavior is not general. Thus from mechanical relaxation studies performed on mixtures of poly(methylmethacrylate) with 1,1-dichlorocyclohexane, Heijboer[4] found that the cyclohexane peak does not appear in those compounds in which there is no difference in the chair-to-chair transition conformers. In agreement with this Karpovich[10] reported that the absorption of the ultrasound presents no maximum in 1,1-dimethylcyclohexane and dioxane, but it presents one in cyclohexyl alcohol and cyclohexylamine. Similar results were reported later by Kotlik et al.[9] for other cyclohexane derivatives.

An important issue in the study of the subglass molecular motions of polymers containing cyclohexylene groups in the main chain is to elucidate whether the subglass relaxation next to the glass–rubber absorption is also caused by flipping motions of the saturated ring. The results at hand are highly controversial. For example, cycloaliphatic and cycloaromatic polyesters in which the glycol residue is 1,4-cyclohexanedimethanol present subglass relaxations that were attributed to molecular motions in which the HC_{cy}–CH_2 bonds of the glycol residue intervene.[6,8] On the contrary, the subglass absorptions were assumed to be the result of flipping motions of the cyclohexylene group in cycloaliphatic polyethers.[2] It can be concluded from the literature results that clear evidence showing that chair-to-chair transitions contribute to the losses was not found in polymers containing cyclohexylene units in their structure.

In this work the mechanical and dielectric relaxations of poly(*cis*/*trans*-1,4-cyclohexanedimethanol-*alt*-formaldehyde) (PCDO) were studied with the aim of gaining a deeper insight into the nature of the relaxation processes in polymers containing cyclohexylene groups in the main chain.

Experimental Section

Materials. Commercial *cis*/*trans*-1,4-cyclohexanedimethanol (30/70) (Eastman Kodak) was acetylated, and by successive crystallizations of the product in *n*-pentane an enrichment in the cis content of the diester that remained in the solution was achieved. A compound with cis content higher than 99% was obtained and was further hydrolyzed. *trans*-1,4-Cyclohexanedimethanol was obtained by two successive crystallizations of commercial glycol from diethyl ether.

Synthesis and Characterization of Cycloaliphatic Polyethers. Three cycloaliphatic polyformals with cis/trans contents of 100/0, 28/72, and 10/90 were obtained by condensation reactions of the corresponding ratios of *cis*/*trans*-glycol with formaldehyde. The reactions were carried out for 48 h under dry nitrogen in refluxing benzene with *p*-toluenesulfonic acid as catalyst. Water was removed from the reaction medium by means of a Dean-Stark distillation trap. The polymers were precipitated with methanol, washed several times with distilled water to eliminate the catalyst, dissolved in benzene, precipitated again with methanol, and finally dried under high vacuum at room temperature.

Although the cis/trans ratio in the polymers was known from the starting compositions of the glycols, the polymers were still characterized by ^1H NMR spectroscopy. The cis/trans ratio for each polymer was determined from the intensities of the doublets centered at 3.31 and 3.43 ppm corresponding to the protons of 1,4 substituted methylene in the cis and trans isomers, respectively.[11]

Table I
Comparison of the Glass Transition Temperature and the Activation Energies Corresponding to Subglass Relaxations in PCDO and PCDS Networks

network	T_g, °C	E_β, kcal/mol mechanical relax.	E_β, kcal/mol dielectric relax.	E_γ, kcal/mol dielectric relax.
cis-PCDO	−4	18.5	18.1	13.2
cis/*trans*(28/72)-PCDO	−4	22		
cis/*trans*(10/90)-PCDO	1	25.5 (β_1) 12.5 (β_2)	17	
cis-PCDS[a]	−40	18.5		8
cis/*trans*(50/50)-PCDS[a]	−38	23		
trans-PCDS[a]	−28	18.5 (β_1) 29 (β_2)		

[a] Taken from ref 8.

Preparation and Characterization of the Networks. Cycloaliphatic polyformal networks were prepared from fractions of number-average molecular weight 6200, 5900, and 6400 with cis/trans content 100/0, 28/72, and 10/90, respectively. Hydroxyl-terminated polymer chains were permitted to react with stoichiometric amounts of 2,4-bis(p-isocyanate benzyl) phenyl isocyanate at 80 °C for 24 h. The soluble fraction of the networks amounted to ca. 10% in all the cases. The glass transition temperature of the amorphous networks was measured with a Du Pont 943 TMA apparatus at a heating rate of 5 °C/min; the values obtained are given in the second column of Table I. X-rays and calorimetric diagrams were obtained with a Philips PW X-ray apparatus in the former case and with a DSC-4 Perkin Elmer calorimeter in the latter.

Mechanical and Dielectric Measurements. Dielectric measurements were performed with a three-terminal cell and a capacitance bridge at several frequencies lying in the range 0.2–100 kHz. The complex permitivity was recorded in 10 °C steps, about 20 min being required to stabilize the temperature in each step. Dynamic mechanical measurements were carried out with a PL-DMTA apparatus at a heating rate of 1 °C/min.

Results

Mechanical and Dielectric Relaxations. Owing to their structural regularity, the cycloaliphatic polyformals used in this study should be crystalline. *trans*-PCDO chains have a relatively high melting point (86 °C), and the crystallization induction time at room temperature is small.[11] However, the induction time increases as the *cis*-cyclohexylene content increases until eventually it becomes infinite for *cis*-PCDO chains. Actually, crystallinity was not detected in these chains kept at 0, 10, 20, and 30 °C for several weeks. For this reason, networks prepared from *cis*-PCDO chains are amorphous. Networks with 28/72 and 10/90 cis/trans cyclohexylene content are also amorphous immediately after quenching from the melt. Even more, crystallinity vestiges were not detected in these latter networks kept at room temperature for more than 1 h after quenching. Mechanical and dielectric experiments were performed on amorphous networks immediatley after quenching, proceeding from low to high temperature. In the case of cis/trans (10/90) PCDO networks, dynamical mechanical experiments were also carried out on samples in which the degree of crystallinity was estimated to be 12%.

The mechanical relaxation behavior of *cis*-PCDO networks is shown in Figure 1. The spectra present a well-developed process centered at 7 °C at 1 Hz, labeled α relaxation, that is associated with the glass–rubber transition, together with a subglass absorption labeled β relaxation and centered at −60 °C at 1 Hz. Moreover, vestiges of a weak and broad relaxation also appear below

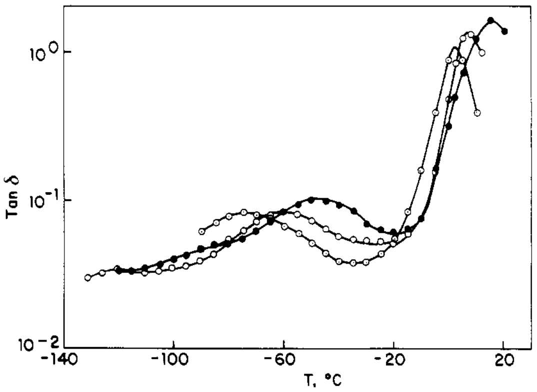

Figure 1. Mechanical loss tangent–temperature plots for amorphous poly(*cis*-1,4-cyclohexanedimethanol-*alt*-formaldehyde) at three frequencies (Hz): (⊙) 0.1, (○) 1, and (●) 10. Results at 0.33 and 3 Hz are not represented for the sake of clarity.

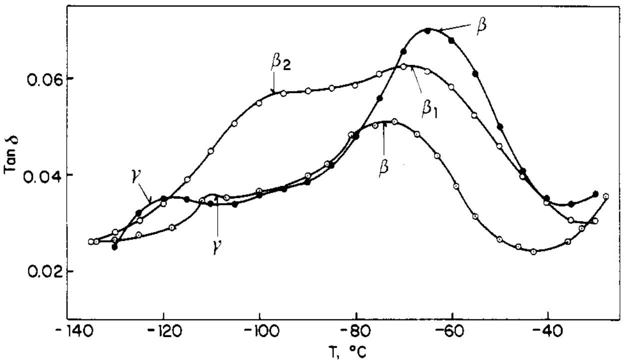

Figure 2. Details of the subglass relaxation spectra at 0.33 Hz for amorphous *cis*-PCDO (●), *cis/trans*(28/72)-PCDO (⊙), and *cis/trans*(10/90)-PCDO (○) networks.

−100 °C; this will be named γ relaxation.

The relaxation spectra of amorphous cis/trans (10/90) PCDO networks also exhibit a strong relaxation whose maximum is located at 8 °C at 1 Hz, ostensibly to be attributed to the glass–rubber transition, followed by a broad and diffuse subglass relaxation extending in a temperature span of more than 100 °C. The relaxation could be the result of two overlapping peaks, one (β_1) centered at −65 °C at 1 Hz and the other (β_2) located at −90 °C. A detailed comparison between the mechanical subglass relaxations at 0.33 Hz corresponding to *cis*-PCDO, *cis/trans*(28/72)-PDCO, and *cis/trans*(10/90)-PCDO networks are shown in Figure 2. It can be seen that the networks with an intermediate *cis*-cyclohexylene content exhibit a β absorption (whose strength has decreased significantly with respect to that of the *cis*- and *trans*-PCDO networks) and two additional diffuse relaxations centered at −95 and −110 °C.

Dynamic mechanical results for crystalline *cis/trans*-(10/90)-PCDO networks are shown as a function of temperature in Figure 3. As expected,[12,13] the strength of the glass–rubber transition decreases, the position of the α absorption is shifted to higher temperature with respect to that of the amorphous network as a consequence of the decrease in chain mobility caused by the crystallites, and the width of the relaxation times distribution increases. The presence of the crystallites also decreases the strength of the secundary relaxations, suggesting that the molecular motions that are involved in the processes take place in the amorphous phase.

Dielectric relaxation results as a function of temperature, at frequencies lying in the range 0.5–50 kHz, are shown for *cis*-PCDO networks in Figure 4. The relaxation spectra present a glass–rubber transition whose strength and width are, respectively, lower and wider than those in the dynamical mechanical absorption. In addition, two subglass relaxations whose maxima at 0.5 kHz are located at −30 (β) and −74 °C (γ) can be detected at low frequencies. As the frequency increases the overlapping between the β and γ absorptions increases, eventually

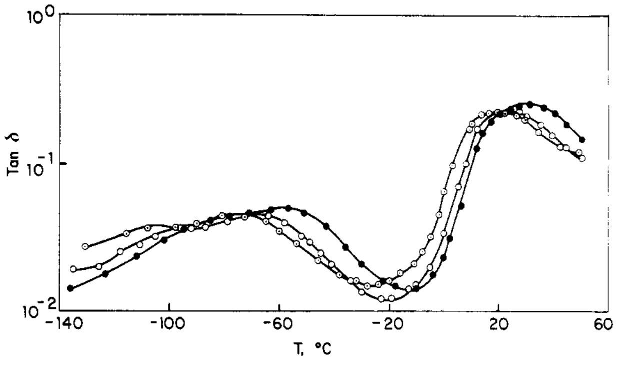

Figure 3. Mechanical relaxation spectra for crystalline cis/trans (10/90) networks at three frequencies (Hz): (⊙) 0.1, (○) 1, and (●) 10.

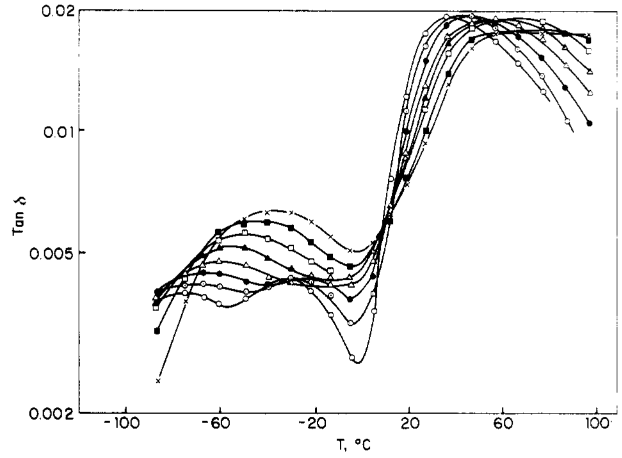

Figure 4. Dielectric loss tangent dependence on temperature for *cis*-PCDO networks at several frequencies (Hz): (×) 100, (■) 50, (□) 20, (▲) 10, (△) 5, (●) 2, (⊙) 1, and (○) 0.5.

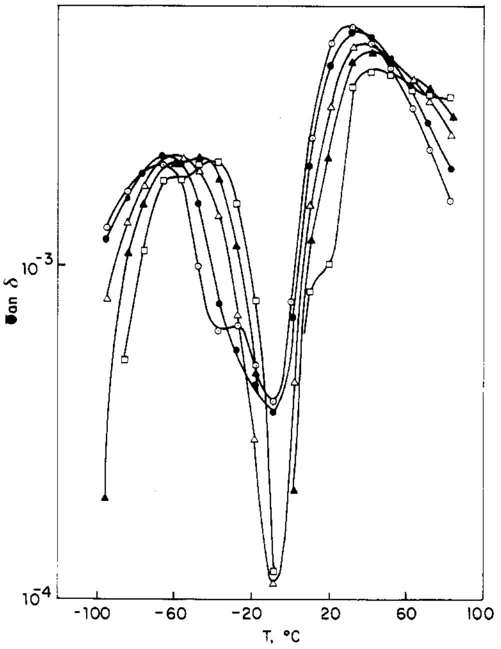

Figure 5. Dielectric relaxation spectra for amorphous *cis/trans*(10/90)-PCDO networks. (See Figure 4 for the values of the frequencies attached to the symbols.)

appearing as a single broad relaxation at frequencies higher than 10 kHz.

Values of the dielectric loss tangent as a function of temperature for *cis/trans*(10/90)-PCDO networks are shown in Figure 5. The spectra present a glass–rubber absorption with maximum located at 28 °C at 1 kHz and two subglass absorptions. A detailed representation of the subglass dielectric relaxations in terms of the loss permittivity shows a small peak (β) in the vicinity of −30 °C followed by other peaks (γ) centered at −70 °C at 1 kHz. It should be pointed out that whereas the subglass dielectric relaxations display lower strength in the networks with higher *trans*-cyclohexylene content, the opposite occurs in the case of the glass–rubber transition. As can be seen in Figures 4 and 5, the intensity of the α dielectric loss tangent decreases from 5.1×10^{-2} for *cis/trans*(10/90)-PCDO to 1.8×10^{-2} for *cis*-PCDO networks, an intermediate value of 2.8×10^{-2} being found for *cis/trans*-(28/72)-PCDO networks.

Influence of the Temperature on the Mechanical and Dielectric Relaxations. The temperature dependence of the relaxation mechanisms that occur in the glassy state was interpreted in terms of the Arrhenius equation

$$\ln \nu = A - E_a/RT_{\max}$$

where ν is the frequency, E_a is the activation energy, and $T_{\max}$ represents the temperature corresponding to the maximum of the absorption at the frequency of measurement. Values of the activation energies obtained by this method for several subglass relaxation processes are given in Table I. In the same table and for comparative purposes are also represented the values of the activation energies involved in the relaxation processes of poly(cyclohexanedimethanol sebacate) (PCSD) networks.[8]

The viscoelastic and dielectric mechanisms associated with the glass–rubber transition are in most systems dependent on the free volume, so that the time τ_i associated with a mechanical or dielectric mechanism i in the relaxation process is related to the relative free volume ϕ by the Doolittle equation[14]

$$\tau_i = A' \exp(B/\phi)$$

where $\phi = (v - v_0)/v_0$, v_0 being the occupied volume in which a relaxation process cannot take place. B is a constant whose value is believed to be close to unity. By assuming that the specific volume v is a linear function of temperature, one obtains the Vogel relationship[15]

$$\ln \tau_i = A + m/(T - T_\infty)$$

where T_∞ is the temperature at which the free volume would be zero were it not for the formation of the glassy state.

As shown in Figure 6, the experimental results fit the Vogel equation reasonably well for $T_\infty = -50$ °C. The relative free volume corresponding to T_g, ϕ_g/B, is related to the slopes of the straight lines of Figure 6 by the equation

$$\phi_g/B = (T_g - T_\infty)/m$$

Values of ϕ_g/B obtained by using this procedure are shown in Table II. It can be seen that the values obtained for ϕ_g/B from mechanical and dielectric experiments are in fair agreement, but they exceed the average value of 0.025 ± 0.005 reported for most systems.[17] Values of ϕ_g larger than 0.030, amounting to 0.033, 0.071, 0.039, and 0.033, have also been reported for polystyrene, poly(dimethylsiloxane), polybutadiene with moderate and high cis content, and ethylene–propylene copolymers, respectively.[17] In all these cases, as well as in the cycloaliphatic polyethers here studied, the large values of ϕ_g/B may be attributed to values of B other than unity as a consequence of differences in the minimum hole size required for local segmental motions. It can be concluded that the free volume interpretation gives a good account of the mechanical and dielectric relaxation processes that take place in the glass–rubber transition of polymer networks prepared from symmetric cycloaliphatic polyethers with cyclohexylene rings incorporated in the main chain.

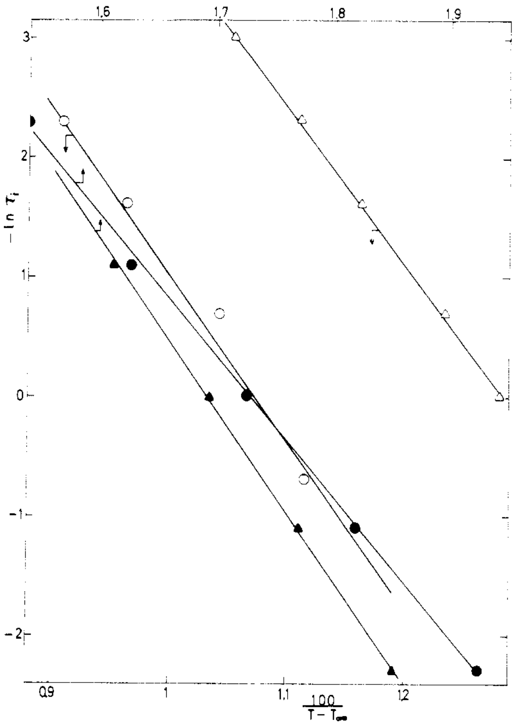

Figure 6. Plot of the logarithm of the relaxation times associated with the maximum of the α peak as a function of $1/(T - T_\infty)$. The symbols ○ and △ represent the dielectric results for *cis*- and *cis/trans*(10/90)-PCDO networks, respectively. Solid symbols represent the mechanical results.

Table II
Comparison of the Values Obtained for ϕ_g/B from the Analysis of the Mechanical and Dielectric Glass–Rubber Relaxations of PCDO and PCDS Networks

network	ϕ_g/B (mechanical)	ϕ_g/B (dielectric)
cis-PCDO	0.039	0.033
cis/trans(28/72)-PCDO	0.036	
cis/trans(10/90)-PCDO	0.037	0.038
cis-PCDS[a]	0.022	0.026
cis/trans(50/50)-PCDS[a]		0.021

[a] Taken from ref 8.

Discussion

Polymers containing cyclohexyl side groups present a prominent mechanical subglass relaxation in the vicinity of −80 °C at 1 Hz, presumably caused by chair-to-chair conformational changes. However, it is not clear whether similar relaxation is exhibited by polymers containing cyclohexylene groups in the main chain. For example, poly(1,4-cyclohexylene ether) (PCE)[2] exhibits at 5260 Hz a strong relaxation peak in the vicinity of −30 °C which was attributed to chair-to-chair flipping motions of the cyclohexylene units. It is obvious that at 1 Hz this relaxation should appear at a much lower temperature, but unfortunately the energy activation of the process, necessary to calculate the value of this displacement in the temperature scale, is not available. The strength of the

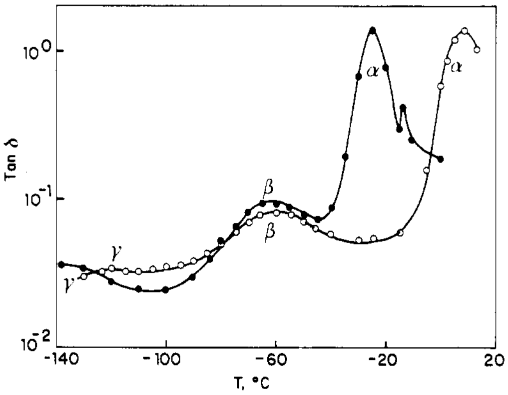

Figure 7. Comparison of the mechanical relaxation spectra obtained at 1 Hz corresponding to poly(*cis*-1,4-cyclohexanedimethanol-*alt*-formaldehyde) (○) and poly(*cis*-1,4-cyclohexanedimethanol sebacate) (●).

relaxation, expressed in terms of tan δ_{max} is somewhat larger than 0.1 and therefore is comparable to the value reported for this quantity in cyclohexyl derivatives. However, the fact that the β relaxation (labeled γ in ref 6) of poly(*cis*/*trans*(32/68)-1,4-cyclohexanedimethanol terephthalate) (PCC) resembles in shape and temperature the β peak of poly(ethylene terephthalate) (PET) has lead Hiltner and Bear[18] to postulate motions around HC_{cy}–CH_2 bonds of the glycol residue, instead of flipping motions of the cyclohexane ring, as the cause of the relaxation.

Comparison of mechanical and dielectric relaxation spectra of networks prepared from the cis and the cis/trans isomers of poly(1,4-cyclohexanedimethanol sebacate) (PCDS)[8] with the corresponding isomers of PCDO may be helpful to elucidate the contribution of the cyclohexylene units to the mechanical and dielectric behavior of cycloaliphatic polymers. In general, PCDO chains are less flexible than PCDS molecules, presumably as a consequence of the strong preference for gauche states that oxymethylenic skeletal bond segments exhibit, which confer rigidity to the former polymers leading to the shifting of the glass transition absorption to higher temperature.[19] This can be seen in Figure 7, where the mechanical relaxation spectra of *cis*-PCDS and *cis*-PCDO networks are shown. The fact that the β mechanical absorptions at 1 Hz of cis isomers of the two polymer networks are centered at the same temperature (~ -60 °C) and that the activation energies of the process are almost the same (see Table I) suggests that the mechanisms responsible for the relaxation processes must involve motions in which the glycol residue, which is the only common moiety in the structural units of the two polymers, takes an active part.

The dielectric relaxation spectra of the cis isomers of PCDS and PCDO at 500 Hz indicate that whereas the proximity of the glass–rubber transition to the relaxation gives rise to the overlapping of the two peaks in the former polymer, the two peaks are clearly separated in PCDO networks as a consequence of their higher glass transition temperature. Since the activation energy of the β dielectric relaxation in PCDO is 18.1 kcal mol^{-1}, the maximum of the absorption at 1 Hz would be located at -65 °C, almost at the same temperature as the mechanical one, suggesting that the same molecular motions produce both relaxations. The strength of the β relaxation of cycloaliphatic polyformals seems to be small in comparison with that of PCDS, presumably as a consequence of the fact that changes in polarity accompanying any transition which intervenes in the alicyclic part of the chains are smaller in PCDO than in PCDS.

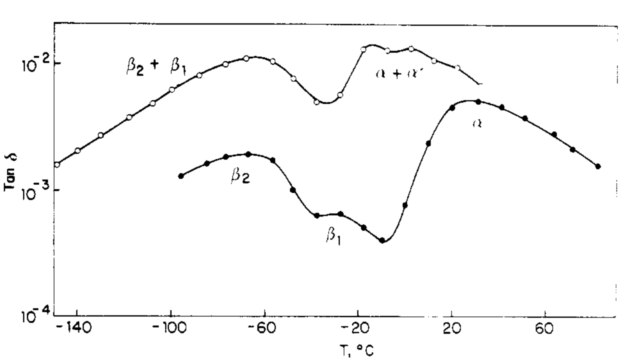

Figure 8. Temperature dependence of the dielectric loss tangent at 1 kHz for semicrystalline PCTS and amorphous *cis*/*trans*-(10/90)-PCDO networks.

The subglass region in the mechanical spectrum at 1 Hz of *cis*/*trans*(10/90)-PCDO networks resembles that of *trans*-PCDS networks in that a broad and diffuse absorption extending in a temperature span of more than 100 °C appears in both cases. A close inspection of Figure 2 reveals that the mechanical subglass relaxations of *cis*/*trans*(28/72)-PCDO networks resemble those of *cis*/*trans*(10/90)-PCDO on the high-temperature side of the spectra, whereas it is more likely to be similar to that of *cis*-PCDO on the low-temperature side. The strength of the absorption on the right side of the spectrum of the first network is lower than that of either the *cis*- or the *cis*/*trans*(10/90)-PCDO networks, and the same occurs on the left side with respect to that of the network with the higher trans content used in this study. This behavior can only be explained by assuming that complex motions involving more than a single structural unit are responsible for the relaxations, so that disruptions of cis···cis or trans···trans sequences, which occur more often when the fractions of *cis*- and *trans*-cyclohexylene units in the copolymers are comparable, should decrease the intensity of the absorptions. Complex motions which intervene in more than a single structural unit were also postulated to explain that the mechanical spectrum of *cis*/*trans*(50/50)-PCDS only presents the β absorption corresponding to the cis isomer and not the β_1 and β_2 peaks corresponding to the trans isomers.[8] Both the *cis*- and the *cis*/*trans*(28/72)-PCDO present a peak centered at -120 and -110 °C, respectively, that is not present in the *cis*/*trans* (10/90)-PCDO network. Therefore, this relaxation, labeled γ, could be associated with motions of segments in which *cis*-cyclohexylene units intervene.

Figure 8 shows the dielectric relaxation spectra at 1 kHz of semicrystalline *trans*-PCDS[8] and amorphous *cis*/*trans*(10/90)-PCDO networks. As was discussed elsewhere[8], the glass–rubber relaxation of the former network is the result of two overlapping α_1 and α_2 peaks, associated with relaxation motions of the dipoles in the free amorphous material of the uncrystallized domains and in the intercrystalline amorphous phase. PCDS networks[8] display a broad subglass relaxation that it is the result of two overlapping peaks (β_1 and β_2), whereas *cis*/*trans*(10/90)-PCDO networks exhibit two relaxations: one whose maximum is is located at -30 °C, associated with motions of segments in which *cis*-cyclohexylene units intervene, and another peak centered at -70 °C at 1 kHz. The temperature at which the maximum of the last absorption would appear at 0.33 Hz, calculated by using the activation energy of 17 kcal mol^{-1} found for this relaxation (see Table I), lies in the vicinity of -100 °C, very close to the temperature at which the β_2 mechanical relaxation is located at the same frequency. This suggests that both the β_2 mechanical and dielectric relaxations are caused by the same type of molecular motions. The strengths of the dielectric glass-rubber relaxation of *cis*-PCDO and the cis/trans copolymers are rather small in comparison with those corresponding to the cis and trans isomers of poly(1,4-cyclohexanedimethanol sebacate),[8] in spite of the fact that dielectric experiments were performed on totally amorphous polymers in the former case and in partially crystalline polymers in the latter. This may be due in part to the difference in polarity between cycloaliphatic polyformals and cycloaliphatic polyesters. In general, gauche states about CH_2–O acetal bonds in the CH_2O–CH_2–OCH_2 sequences of PCDO chains have an energy ca. 1.2 kcal mol^{-1} below that of the alternative trans states. Consequently, there is a high fraction of $g^{\pm}g^{\pm}$ conformations about two consecutive acetal bonds, and here the dipoles associated with the CH_2OCH_2 groups are placed in an almost antiparallel direction. These conformations do not contribute to the dipole moment of the chains, and hence the low polarity of PCDO networks, independently of the cis/trans content. Actually, the dipole moment of these polymers, expressed in terms of the dipole moment ratio $\langle\mu^2\rangle/nm^2$ ($\langle\mu^2\rangle$ is the mean-square dipole moment of the chains and nm^2 the value of this quantity for a freely jointed chain of similar number of skeletal bonds) is only[20] 0.167. This value contrasts with the values of 0.983 and 0.631 found for the cis and trans isomers of poly(1,4-cyclohexanedimethanol sebacate),[21] respectively.

Concluding Remarks

The results discussed above seem to suggest that the β relaxations in PCDO networks, both cis and cis/trans, are produced by complex molecular motions involving more than a single structural unit. The fact that the activation energy for the mechanical and dielectric relaxations is similar in both cases and its value is significantly larger than 11.5 kcal mol^{-1}, the energy involved in the chair-to-chair inversion, strongly supports the assumption that conformational changes in the skeletal bonds of the acyclic part of the chains, rather than cyclohexylene flipping motions, are the cause of the relaxation.

Acknowledgment. This work was supported by the CAICYT and the CICYT through Grants No. 84/0493 and PB86-0620.

Registry No. *cis*-PCDO, 117942-62-8; *trans*-PCDO, 117942-63-9.

References and Notes

(1) Ishida, Y.; Yamafuji, K. *Kolloid. Z. Z. Polym.* **1961**, *177*, 97.
(2) Baccareda, M.; Magagnini, P. L.; Giusti, P. *J. Polym. Sci. A-2* **1971**, *9*, 1341.
(3) Frosini, V.; Magagnini, P. L.; Butta, E.; Baccared, M. *Kolloid Z. Z. Polym.* **1966**, *213*, 115.
(4) Heijboer, J. *TNO Communication* **1972**, no. 435.
(5) Heijboer, J. *Molecular Basis of Transitions and Relaxations*; 1984; p 277.
(6) Hiltner, B. E. *J. Macromol. Sci. Phys.* **1972**, *B6*, 545.
(7) Chapoy, L. L.; Kops, J. *J. Polym. Sci., Polym. Lett. Ed.* **1973**, *11*, 515.
(8) Diaz-Calleja, R.; Gômez, J. L.; Ribes, A.; Riande, E.; Guzmân, J. *Macromolecules*, in press.
(9) Kotlik, P.; Heidingsfeld, V.; Zelinger, J. *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 1417.
(10) Karpovich, J. *J. Chem. Phys.* **1954**, *22*, 1767.
(11) Riande, E.; Guzmân, J.; Saiz, E.; Tarazona, M. P. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 1031.
(12) Boyd, R. H. *Polymer* **1985**, *26*, 323.
(13) Boyd, R. H. *Polymer* **1985**, *26*, 1123.
(14) Doolittle, A. K.; Doolittle, B. D. *J. Appl. Phys.* **1957**, *28*, 901.
(15) Vogel, H. *Physik.* **1921**, *22*, 645.
(16) Plazek, J. D.; O'Rourke, V. M. *J. Polym. Sci. A-2* **1971**, *9*, 208.
(17) Ferry, J. D. *Viscoelastic Properties of Polymers*; Interscience: New York, 1981.
(18) Illers, K. H.; Breuer, H. *J. Colloid Sci.* **1963**, *1*, 18.
(19) Riande, E. *Makromol. Chem. Macromol. Symp.* **1986**, *2*, 179.
(20) Riande, E.; Guzmân, J.; Saiz, E. *Polymer* **1981**, *21*, 465.
(21) Riande, E.; Guzmân, J.; de la Campa, J. G.; de Abajo, J. *Macromolecules* **1985**, *18*, 1553.

In Situ Sequential Polyurethane/Poly(methyl methacrylate) Interpenetrating Polymer Networks: Structure and Elasticity of Polyurethane Networks

M. T. Tabka,* J. M. Widmaier, and G. C. Meyer

Institut Charles Sadron (CRM-EAHP), Ecole d'Application des Hauts Polymères, 4, rue Boussingault, 67000 Strasbourg, France.
Received May 10, 1988;
Revised Manuscript Received October 10, 1988

ABSTRACT: As part of a study concerning polyurethane/poly(methyl methacrylate) interpenetrating polymer networks (IPNs), polyurethane networks were synthesized at various dilutions of the reaction medium and at different values of the NCO/OH ratio. The network defects arising in such materials were evaluated by three independent experimental approaches: solvent extraction, swelling behavior, and elastic modulus. It was found that networks with the least defects are formed at high precursor concentration, with a NCO over OH excess of about 7%. Different theories leading to the structural parameters of polymer networks were utilized and corroborate well with the experimental results. The study provides a means of classification of these polyurethane networks according to the amount of their defects; furthermore, it allows one to investigate the influence of the network formed first on the formation of the second network in sequential IPNs, and consequently on the ultimate properties of the material.

Introduction

Polymers may be combined in different ways, but due to their mutual incompability, they tend to a more or less pronounced phase separation. From an industrial point of view, interpenetrating polymer networks (IPNs),[1–4] in which the polymers coexist in the form of their physically entangled networks, are very interesting materials. However, such combinations are quite complicated to study, and only few of the usual investigation methods are suitable for the study of IPNs. This explains why general structure–properties relationships have not yet been established. Only their synthesis and some application-oriented properties are usually described in the literature. Also, the chemical aspects of the formation of an IPN, like the kinetics, the viscosity, the compability changes, ..., have rarely been reported.

0024-9297/89/2222-1826$01.50/0