(7) Cowie, J. M. G.; Wu, H. H. *Br. Polym. J.*, in press.
(8) Shimizu, K.; Yano, O.; Wada, Y. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 1959.
(9) Boyer, R. F. *Rubber Chem. Technol.* **1963**, *36*, 1303.
(10) Boyd, R. H.; Breitling, S. M. *Macromolecules* **1974**, *7*, 855.
(11) Cowie, J. M. G.; *J. Macromol. Sci., Phys.* **1980**, *B18*, 569.
(12) Dale, J. *Pure Appl. Chem.* **1971**, *25*, 469.
(13) Dunitz, J. D.; Seiler, P. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1974**, *30*, 2739.
(14) Curtis, A. J. *J. Res. Natl. Bur. Stand., Sect. A* **1961**, *65A*, 185.
(15) Woodward, A. E.; Sauer, J. A.; Deeley, C. W.; Kline, D. E. *J. Colloid. Sci.* **1957**, *12*, 363.

Mechanical and Dielectric Relaxations in Cycloaliphatic Polyester Networks

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ABSTRACT: Dielectric and mechanical loss tangent measurements performed on networks prepared from the cis (PCCS), trans (PTCS), and cis/trans (50/50, PCC) isomers of poly(oxymethylene-1,4-cyclohexylenemethyleneoxysebacoyl) present a well-defined α absorption associated with the glass–rubber transition, whose location and strength depends on the presence of crystallites on the samples. The α mechanical absorption at 1 Hz corresponding to amorphous PCCS and PCC networks is centered at −26 °C in both cases; however, the maximum of the peak is shifted to −17 °C for PTCS networks quenched from the melt. Only a weak dielectric α process is detected at low frequencies in the latter networks due to the presence of crystallites that presumably preclude the possibility that amorphous-phase dipoles can relax over all directions. Two subglass mechanical relaxations labeled β and γ and located at −60 and −140 °C (at 1 Hz), respectively, appear in both PCCS and PCC networks, whereas the relaxation spectra of PTCS networks present at 0.1 Hz a broad subglass β absorption that can be resolved in two overlapping peaks centered at −80 (β_1) and −105 °C (β_2). The fact that the mechanical relaxation spectra of PCCS and PCC are similar suggests that the β relaxation in PTCS must be associated with molecular motion modes involving more than two structural units. However, the dielectric loss tangent versus temperature plot of PCC presents in the subglass region all the absorptions corresponding to the parent homopolymers. The critical interpretation of the dielectric relaxation behavior of the networks indicates that subglass dielectric absorptions are probably caused by conformational changes that take place in the glycol residue, whereas the mechanical responses may be caused by molecular motions in which conformational changes take part that involve skeletal bonds beyond those of the glycol residue.

Introduction

In recent years attention has been paid to the studies of relaxation phenomena in aliphatic polyesters after a long period of relative neglect.[1-8] These systems show a well-developed glass–rubber transition that in some cases, owing to the relative low melting point of some members of the family, tend to interfere with the observation of crystalline α_c processes; consequently, the notation β is used to denote this transition. Below the β peak another prominent absorption appears, labeled γ, that can extend over an interval of temperature of ca. 100 °C, and its behavior is similar to the γ processes in polyethylene. Most of the investigations in these polymers were undertaken with the aim of elucidating the nature of the molecular motions that occurring either in the amorphous or in the crystalline phases give rise to the mechanical and dielectric relaxations observed in polymers in general.[6]

An important family of polyesters, from a basic point of view, is the one formed by polymers obtained by condensation of aliphatic diacids and glycols containing a cyclohexane residue in their structure.[9,10] The mechanical and dielectric properties should be strongly dependent on both the conformations of the cyclohexane ring and the relative positions of the carbon atoms in the cyclohexane in which the substitution of the hydrogen atoms is performed. Although three conformations (chair, boat, and skew) are possible for cyclohexane, it seems that this ring in the cycloaliphatic polyesters is in the chair form.[9,10] In the case of 1,4-disubstituted cyclohexanes, the equatorially substituted chair forms give rise to the trans isomers, whereas cis isomers are obtained if the substitution is equatorial/axial.

This work describes the results obtained from isocronal experiments performed on model networks prepared from the cis, trans, and copolymers cis/trans isomers of poly(oxymethylene-1,4-cyclohexylenemethyleneoxysebacoyl) (PCS) chains. Attempts have also been made to establish the molecular interpretation of the relaxations observed.

Experimental Section

Synthesis of the Polyesters. Hydroxyl-terminated chains of poly(oxymethylene-1,4-*trans*-cyclohexylenemethyleneoxysebacoyl) (PTCS), poly(oxymethylene-1,4-*cis*-cyclohexylenemethyleneoxysebacoyl) (PCCS), and the copolymer (50/50) of poly(oxymethylene-1,4-*cis*/*trans*-cyclohexylenemethyleneoxysebacoyl) (PCC) were obtained by condensation of sebacic acid with the corresponding isomers of 1,4-cyclohexanedimethanol. The polymerization was carried out in xylene solutions by using the procedure described elsewhere.[9] The glycol trans isomer had previously been isolated from the commercial mixtures of cis and trans (30/70) isomers by recrystallization from ethyl acetate. In the same way, 1,4-*cis*-cyclohexanedimethanol had been obtained by acetylation of commercial 1,4-cyclohexanedimethanol with acetic anhydride by using the method given in ref 9. The all-planar conformations of the repeating units of PTCS and PCCS are shown in Figure 1.

Preparation of the Networks. PTCS, PCCS, and PCC chains of number-average molecular weights 6000, 7200, and 6800, re-

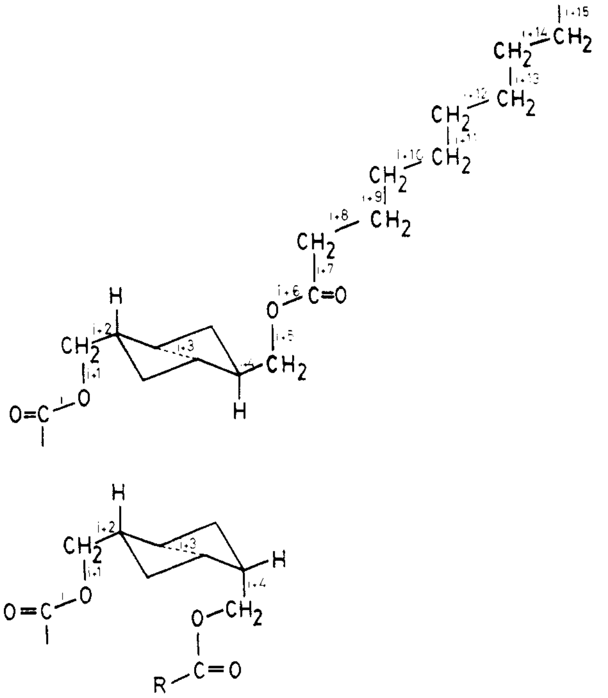

Figure 1. Structural units of the cis and trans isomers of poly(oxymethylene-1,4-cyclohexylenemethyleneoxysebacoyl) in all-trans conformations.

spectively, were used to prepare model networks by end-linking the hydroxyl-terminated chains with equimolecular amounts of 2,4-bis(*p*-isocyanatobenzyl)phenyl isocyanate. The soluble fractions of PTCS, PCCS, and PCC networks amounted to 11%, 9%, and 11%, respectively.

The glass transition temperature of both amorphous PCCS and slightly crystallized PTCS networks, measured with a Du Pont 943 TMA apparatus at a heating rate of 5 °C/min, was −40 and −28 °C, respectively. The value of T_g for PCC was also found to be −38 °C. In some experiments PCCS and PTCS networks were used that were crystallized from the melt at 20 °C for 7 days; the melting temperatures of these networks, measured with a Perkin DSC-4 calorimeter at 5 °C/min, were 40 and 59 °C, respectively. It should be pointed out that the melting temperatures of the uncross-linked PCCS and PTCS chains, measured in the same conditions, were 48 and 70 °C, respectively. PCC networks, kept at 20 °C for several weeks, did not crystallize.

Relaxation Measurements. Dynamic mechanical measurements were performed with a PL-DMTA apparatus at a heating rate of 1 °C/min. Dielectric measurements were carried out with a three-terminal cell and a capacitance bridge (General Radio, Type 1620 A) at nine frequencies lying in the range 0.2–100 kHz. The dielectric measurements were made from low to high temperatures in 10 °C steps; about 20 min were required to stabilize the temperature in each step.

Experimental Results

Mechanical Relaxations. The crystallization of PCCS networks, described in detail elsewhere,[11] shows that the reciprocal of the time required to achieve 10% of the total crystallinity attainable presents a maximum at 0 °C, ca. 40 °C below the melting temperature of the crystallized networks. As is easily understood, a decrease in temperature initially increases the crystallization rate because of the increase in undercooling but decreases it as the polymer becomes sluggish and approaches the glassy state. The crystallization rate at −20 and 13 °C is almost similar in such a way that 10% of the total crystallinity is achieved in ca. 500 min; however, this time reduces to only 100 min, if the network crystallizes at 0 °C. The networks quenched in liquid nitrogen from the melt do not exhibit crystallization vestiges at all. On the contrary, quenched PTCS networks show weak signs of crystallinity. Since the total crystallinity developed in PTCS and PCCS uncross-linked chains amounts to 40% and 35%, respectively,[11] it is expected that the total crystallinity attainable in the networks should be lower. By comparing the melting enthalpies of both PTCS and PCCS networks with those of the respective 100% crystalline chains,[12] one obtains for the crystallinity of the networks with different thermal histories the values shown in Table I.

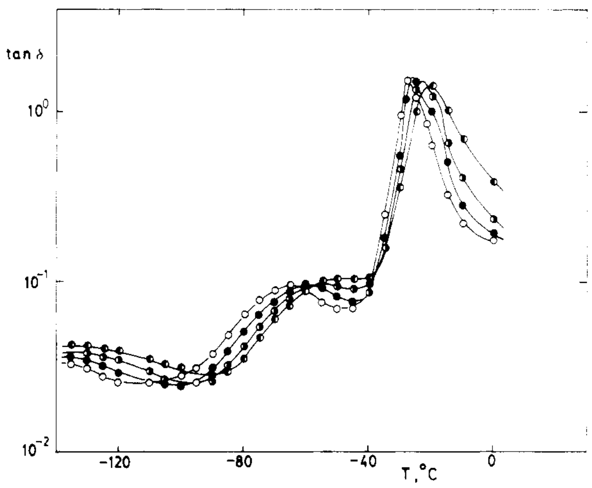

Figure 2. Mechanical loss tangent dependence on temperature, at several frequencies, for amorphous poly(oxymethylene-1,4-cyclohexylenemethyleneoxysebacoyl) (PCCS) networks: (○) 0.33, (●) 1, (◑) 3, and (◐) 10 Hz.

Table I
Crystallinity of PCCS, PTCS, and PCC Networks

network	thermal history	crystallinity, %
PCCS	quenched from the melt in liquid nitrogen	0
PCCS	7 days at 20 °C	~18
PTCS	quenched from the melt in liquid nitrogen	vestiges (<1)
PTCS	7 days at 20 °C	~16
PCC	7 days at 20 °C	0

Dynamic mechanical results at four frequencies (0.33, 1, 3, and 10 Hz), obtained from low to high temperatures on amorphous PCCS networks, are shown in Figure 2. Like the aliphatic polyesters and polyamides,[4,8] the cycloaliphatic polyester shows a well-developed process centered at −26 °C (at 1 Hz), named α, ostensibly to be attributed to the glass–rubber relaxation. Two subglass relaxations, labeled β and γ, can be seen in the relaxation spectrum. The first one, centered at −60 °C (at 1 Hz), although weaker than the α relaxation is still prominent, and it overlaps with this relaxation at frequencies higher than 1 Hz. The γ relaxation appears as a well-defined and broad relaxation below −100 °C.

A close inspection of the α relaxation in Figure 3 reveals the presence of a small peak centered at −14 °C that is attributed to incipient crystallization developed in the networks above −20 °C. The effect of crystallinity in the shape of the peak is also shown in Figure 3, where the dynamic mechanical behavior of PCCS networks crystallized under and without orientation is represented. As occurs in other crystalline systems,[8,13,14] the temperature of the process is displaced upward, the width of the relaxation is much broader than in the amorphous one, and the intensity of the peak decreases. This behavior is a consequence of the fact that crystals restrict the generalized long-range segmental motions in the amorphous phase that are characteristic of a glass transition.[13,14] The fact that the intensity of the peak is slightly higher in the

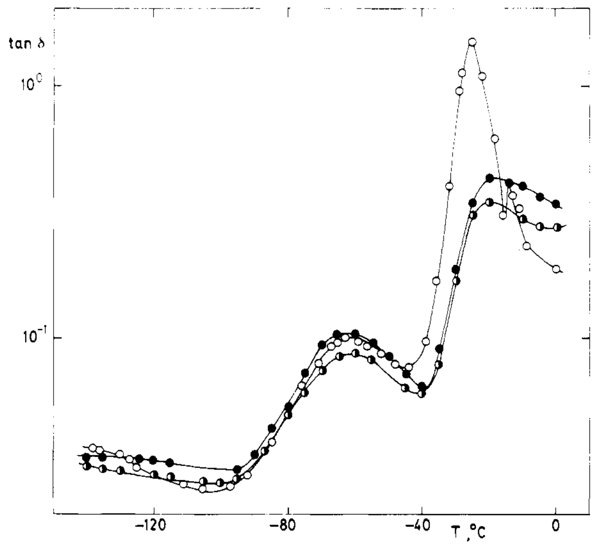

Figure 3. Effect of crystallinity and orientation on the dependence of the mechanical loss tangent on temperature for poly(oxymethylene-1,4-*cis*-cyclohexylenemethyleneoxysebacoyl) networks, at 1 Hz: (○) amorphous network; (●) crystallized network at 20 °C for 7 days; (◐) crystallized network under an elongation ratio of 1.24.

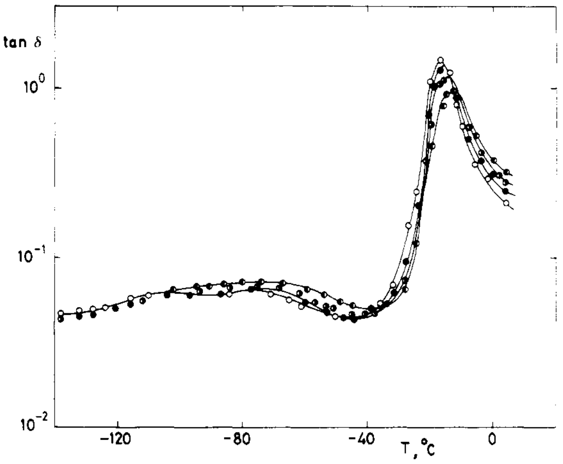

Figure 4. Dynamic mechanical loss tangent for poly(oxymethylene-1,4-*trans*-cyclohexylenemethyleneoxysebacoyl) (PTCS) networks quenched from the melt, at several frequencies. (See Figure 2 for the values of the frequencies attached to the symbols indicated.)

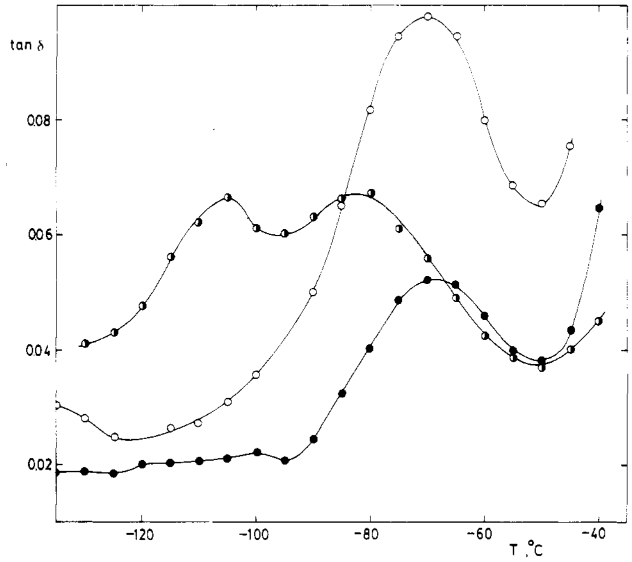

Figure 5. Subglass relaxations of the cis (○), trans (◐), and cis/trans (50/50) (●) isomers of poly(oxymethylene-1,4-cyclohexylenemethyleneoxysebacoyl) at 0.1 Hz; the two first networks were quenched from the melt.

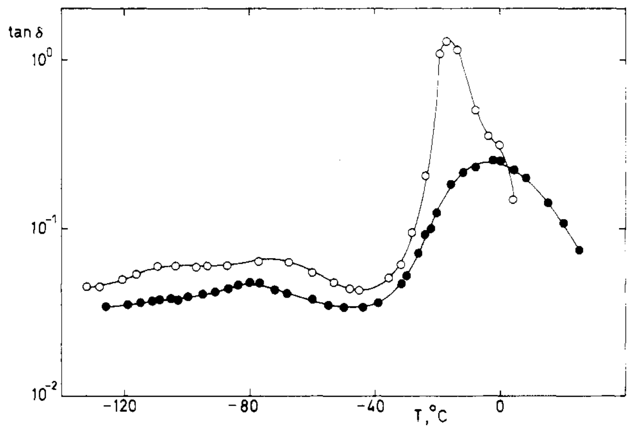

Figure 6. Mechanical relaxation spectrum at 1 Hz of PTCS networks quenched from the melt (○) and crystallized at 20 °C for 7 days (●).

crystallized nonoriented network than in the oriented one suggests that the orientation of the amorphous phase in the latter networks suppresses some conformations involved in the molecular motions that give rise to the relaxation process.

An important characteristic of the β subglass relaxation is that it is broader than the glass–rubber and overlaps with this process. Moreover, the shape and location of the β relaxation are apparently insensitive to the presence of crystallites but are slightly dependent on the orientation of the amorphous phase. Again, the lower intensity of the peak corresponding to the oriented networks seems to suggest that the conformations that give rise to this relaxation are somewhat restricted. In any case the almost null dependence of the strength of the peak on the crystallinity of unoriented networks is in consonance with the fact that the process must be associated with molecular motions in the amorphous phase of localized character.[14]

Because of experimental difficulties, mechanical loss tangent versus temperature results were not obtained below −140 °C; consequently, the shape of the γ relaxation of PCCS networks could not be registered in its totality. It should be pointed out, however, that the data at hand indicate that the strength of the absorption is significantly lower than that corresponding to the previous ones and, at the same time, the orientation and crystallinity of chains also decrease the strength of the relaxation process.

The relaxation behavior of quenched PTCS networks, represented in Figure 4, shows a prominent relaxation centered at −17 °C (at 1 Hz) followed by a diffuse and broad relaxation that extends from ∼−50 to ∼−130 °C. The strength and width of the first peak are comparable to that exhibited by the glass–rubber transition in amorphous PCCS, and also it is the result of long-range motions in the amorphous phase. Therefore, the notation α is used for this relaxation. As can be seen in Figure 5, the subglass relaxation can be resolved in two overlapping peaks centered at ca. −80 °C (β_1) and at −105 (β_2, at 0.1 Hz).

The dynamic relaxation spectrum of PTCS networks, crystallized at 20 °C for 7 days, is represented in Figure 6. As usual, the α absorption is shifted to higher temperature, the relaxation strength decreases, and the width of the absorption increases with respect to the α relaxation of the slightly crystallized network. Moreover, the intensity of the β peak decreases, indicating again that the

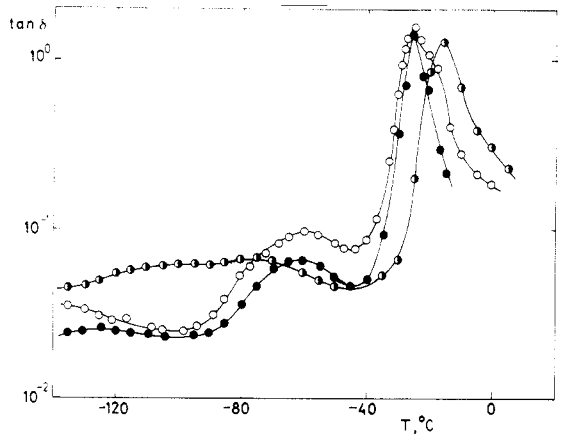

Figure 7. Temperature dependence of the mechanical loss tangent on temperature, at 1 Hz, for networks synthesized from the cis (○), trans (◐), and cis/trans (50/50) (●) isomers of poly(oxymethylene-1,4-cyclohexylenemethyleneoxysebacoyl); the two first networks were quenched from the melt.

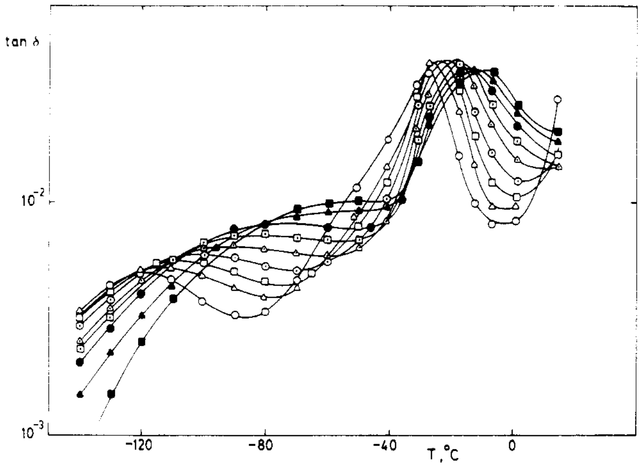

Figure 8. Temperature dependence of the dielectric loss tangent on temperature for amorphous PCCS networks at several frequencies: (○) 0.2, (△) 0.5, (□) 1, (⊙) 2, (◬) 5, (⊡) 10, (●) 20, (▲) 50, and (■) 100 kHz.

crystallites hinder the molecular motions involved in the process. Consequently, the β relaxation must take place mainly in the amorphous phase.

Comparison of the relaxation behavior of cis, trans, and cis/trans (50/50) isomers of poly(oxymethylene-1,4-cyclohexylenemethyleneoxysebacoyl) is shown in Figure 7. It can be seen that the relaxation spectrum of the copolymer is similar to that of the cis isomer, since the α and β absorptions are located at the same temperature as the corresponding relaxations in PCCS. The absence of crystallinity development in the copolymer during the dynamic mechanical measurements causes the α relaxation to be more symmetrical and its width to be narrower than for this relaxation in PCCS and PTCS. The β peak, significantly lower in intensity than this peak in the cis isomer, does not show any contribution from the trans isomer units present in the chains. The γ absorption that appears in PCCS is also observed in the copolymer.

Dielectric Relaxations. Values of the dielectric loss tangent as a function of temperature for quenched PCCS, PTCS, and PCC are shown in Figures 8–10, respectively, at nine frequencies from 0.2 to 100 kHz. An examination of the relaxation spectrum obtained at 0.2 kHz on the initially amorphous PCCS networks reveals a prominent α peak associated with the glass–rubber transition, centered at the same temperature as the α mechanical relaxation determined at 1 Hz. Moreover, a small shoulder can be detected on the low-temperature side of the α relaxation (at ca. -50 °C) that presumably is the result of the overlapping of the α and β peaks. Finally, a well-developed γ relaxation appears at roughly the same temperature as the mechanical one. Summing up, the dielectric relaxation spectra of PCCS present absorption peaks at low frequencies that are located at roughly the same temperatures as in the dynamic mechanical spectra. It should be stressed, however, that at frequencies above 1 kHz, both the β and γ peaks are shifted to higher tem-

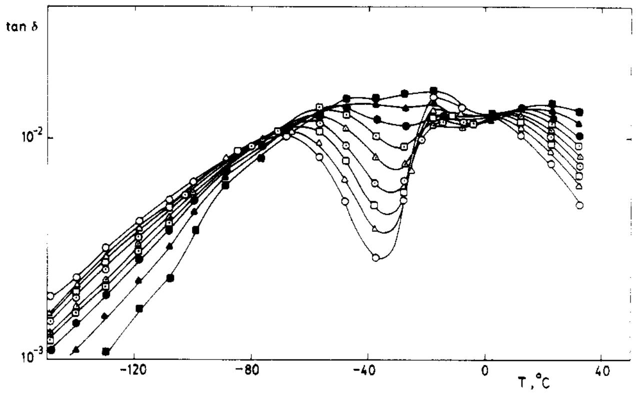

Figure 9. Dielectric relaxation spectrum for PTCS networks, quenched from the melt at several frequencies. (See Figure 8 for the values of the frequencies attached to the symbols indicated.)

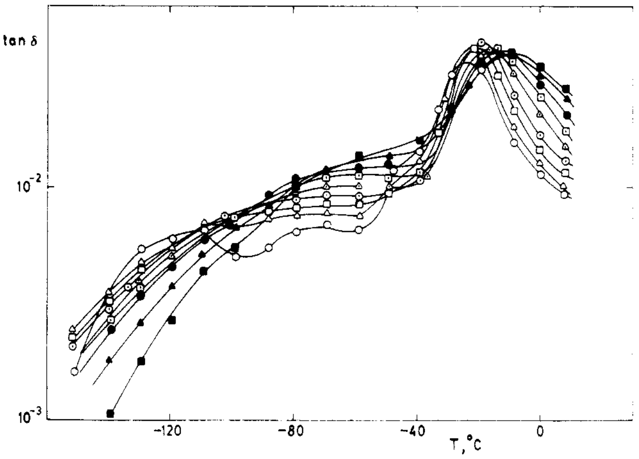

Figure 10. Temperature dependence of the dielectric loss tangent on temperature, at several frequencies, for networks prepared from poly(oxymethylene-1,4-cis/*trans*-cyclohexylenemethyleneoxysebacoyl) (50/50) chains. (See Figure 8 for the values of the frequencies attached to the symbols indicated.)

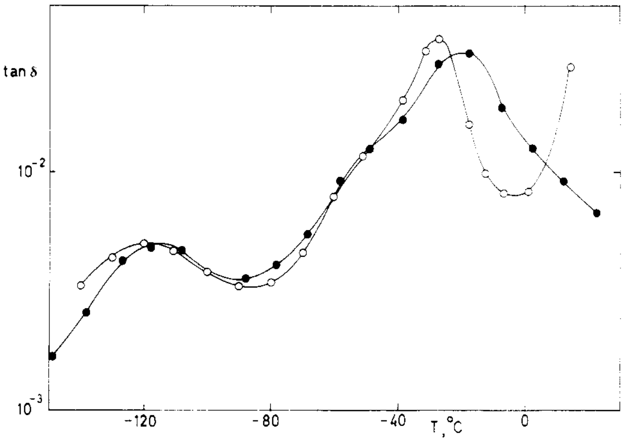

Figure 11. Dielectric loss tangent at 0.2 kHz for the amorphous PCCS networks (○) and the same networks crystallized at 20 °C for 7 days (●).

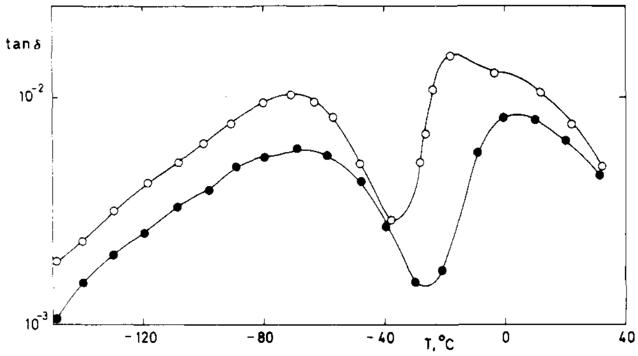

Figure 12. Dielectric loss tangent at 0.2 kHz for PTCS networks quenched from the melt (○) and the same networks crystallized at 20 °C for 7 days (●).

peratures and consequently overlap with the α relaxation.

Comparison of the dielectric relaxation spectra of amorphous and crystalline PCCS networks at 0.2 kHz is shown in Figure 11. The similarities between the two spectra are higher than in the case of the mechanical ones. It can be seen that crystallinity slightly decreases the intensity of the α absorption, and it shifts a few degrees upward the maximum of the peak. The β relaxation is clearly detected in the crystalline network as a consequence of the fact that the α relaxation is shifted to higher temperature. The intensity and location of the γ absorption are not affected by the presence of crystallites in the networks.

The dielectric loss tangent versus temperature plot for quenched PTCS, shown in Figure 9, presents a broad β subglass process with a low-temperature side shoulder, suggesting that as in the case of the mechanical relaxation, the β peak is the result of two overlapping absorptions, one centered in the vicinity of −110 °C at 0.2 kHz and the other at −70 °C, almost 10 °C above the β_1 mechanical peak.

Owing to the slowness in fitting in the capacitance cell the PTCS network quenched from the melt, significant crystallization develops in the samples. An inspection of the glass–rubber relaxation peak in Figures 9 and 12 reveals that the peak might be the result of two overlapping peaks centered in the vicinity of −20 and 0 °C, respectively. This phenomenon suggest that crystallinity may be so incompletely developed that crystalline entities are not fully impinged and presumably two types of amorphous material exist simultaneously: free or unconstrained and intercrystalline constrained. Consequently two peaks, named α and α', could be associated to relaxation motions of the dipoles in the free amorphous material of the uncrystallized domains and in the intercrystalline amorphous phase, respectively. Similar behavior occurs in poly(ethyleneterephthalate) (PET).[15] The dielectric relaxation spectrum of the PTCS network crystallized at 20 °C, obtained at 0.2 kHz, is shown in Figure 12. By comparing this spectrum with that obtained on the initially quenched sample, one can see that the intensity of the β peak decreases as the crystallinity increases, the α peak is not detected, and only a prominent α' relaxation is present.

An important characteristic of the dielectric loss tangent versus temperature plot corresponding to the copolymer is that at difference with the mechanical spectrum it presents at low frequencies all the relaxations that appear in the parent homopolymers. As can be seen in Figure 10, the spectrum at 0.2 kHz presents a glass–rubber relaxation whose temperature at the loss maximum is located at −24 °C; the relaxation shows in turn a pronounced low-temperature side shoulder at ca. −44 °C that corresponds to the β peak of the cis component. Another relaxation centered at −70 °C corresponds to the β_1 peak of the trans isomer, and the broad relaxation below −95 °C is the result of overlapping the β_2 absorption of the trans units and the γ relaxation of the cis component.

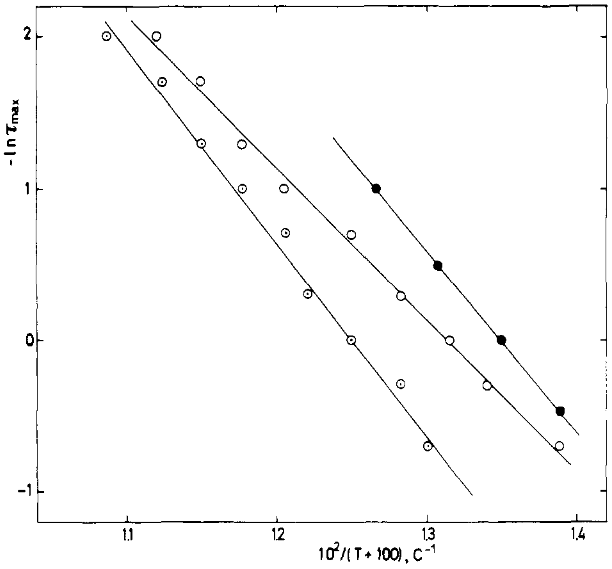

Figure 13. Plot of the logarithm of the relaxation times associated to the maximum of the α peak as a function of $1/(T + 100)$; dielectric results for the copolymer PCC (⊙) and amorphous PCCS (○); (●) mechanical results for amorphous PCCS networks.

Temperature Dependence of the Relaxation Times. To investigate whether the α process is really associated with a change in free volume as occurs in the glass transition, we assumed that the relaxation time τ_i, associated with a mechanism i, is related to the free volume by the Doolittle equation[16]

$$\tau_i = A \exp(B/\phi) \qquad (1)$$

where B is a constant whose value is believed to be 1, and $\phi = (v - v_0)/v_0$ is the relative free volume, v_0 being the occupied volume. The Doolittle equation leads to the Vogel expression[17]

$$\log \tau_i = \log A' + (m/2.303)/(T - T_\infty) \qquad (2)$$

if the assumption is made that the volume v linearly increases with temperature in accordance with

$$V = V_0 + \alpha_f(T - T_\infty) \qquad (3)$$

where T_∞ is the temperature at which the free volume would be zero were it not for the formation of the glassy state.[18,19] Accordingly, if the volume governs the process, plots of the logarithm of the inverse of the frequency against the temperature at which the loss maximum appears should be a straight line. Plots of this kind for the mechanical and dielectric α relaxations of PCCS and for the dielectric α process of PCC are shown in Figure 13. Unfortunately, the α mechanical relaxation of the copolymer could not be studied because we only dispose of loss tangent data at a single frequency. Moreover, it was not advisable to proceed with this analysis in PTCS because significant crystallization occurs in the networks.

Since fitting of experimental results to eq 2 requires a choice of T_∞, trials were made until curvature was mostly eliminated by using the rule of thumb that this parameter is usually about 50 °C below the glass transition; thus $T_\infty = -100$ °C was found for PCCS and PCC, respectively. The value of m in eq 2 is related to the free volume at T_g by the equation[18]

$$m = (B/\phi_g)(T_g - T_\infty) \qquad (4)$$

Table II
Activation Energies E_a (in kcal mol^{-1}) Associated with the Mechanical Subglass Relaxations for PCCS, PTCS, and PCC Networks

network	$E_a(\beta)$	$E_a(\gamma)$
PCCS	18.5	8 (6)[a]
PTCS	18.5 (β_1) 29 (β_2)	
PCC	23	

[a] The quantity in parentheses represents the value of E_a for the dielectric relaxation.

Values of $\phi_g/B = 0.026$ and 0.022 were calculated from the analysis of the dielectric and mechanical results of PCCS, respectively, in good agreement with the value of 0.025 ± 0.005 reported for most amorphous polymers;[19] the value $\phi_g/B = 0.021$ is obtained from the dielectric results of the copolymer. In view of these results it can be concluded that the α processes in the amorphous polyesters is governed by the volume.

Values of the activation energies E_a associated with the β and γ relaxations, obtained from Arrhenius plots, are shown in the second and third columns of Table II. It is worthy to note that the activation energy involved in both dielectric and mechanical γ processes in PCCS is similar. However, the activation energies associated with the β processes in PCCS and PTCS are somewhat larger than those reported for similar relaxations in aliphatic polyesters, suggesting that the relaxations could involve molecular motions in which the bulky cyclohexane ring intervenes.

Discussion

Although the glass–rubber relaxation at low frequencies is obviously dependent on intramolecular and intermolecular interactions, transitions that occur at high temperature suggest relatively high barriers to bond rotations. In other words, the glass–rubber transition is straightforwardly connected to chain flexibility. Conformational flexibility per skeletal bond of a chain of N skeletal bonds may be expressed in terms of the conformational partition function by the equation[20]

$$z = Z^{1/N} \tag{5}$$

However, since Z depends on the conformation chosen as reference, chain flexibility may alternatively be expressed by the conformational entropy S, which is related to z by the relationship[20,21]

$$S = R(\ln z + (T/z)\, \mathrm{d}z/\mathrm{d}T) \tag{6}$$

which is independent of the reference state chosen for its evaluation. Values of S were obtained by using the conformational energies described in detail elsewhere.[9,10] The results obtained for S at 30 °C were 1.38 and 1.39 cal/(mol K) for PCCS and PTCS, respectively. The closeness of these values suggests that the glass–rubber relaxation should take place in roughly the same interval of temperature in both cases. The fact that the glass–rubber relaxation for the cis isomer occurs at a slightly lower temperature than for the trans isomer is partially a consequence of the presence of crystallinity in the latter polymers that can affect the transition in an unpredictable manner.

Comparison of the relaxation behavior to that of the cis (PCCT), trans (PCTT), and cis/trans (28/72 PTCT) isomers of poly(1,4-cyclohexylenedimethyleneterephthalate) (PCT)[22] is especially important to assign the molecular motions that give rise to the subglass relaxations found in the polymers described in the present work. The cis-cycloaromatic isomer (PCCT) shows a strong mechanical γ peak at −73 °C (at 1 Hz), and this relaxation is shifted to −95 °C in the case of the trans isomer (PCTT).[22] Moreover, the copolymer PTCT presents a composite γ peak, which can be resolved in two components associated to the cis and trans glycols. It is worthy to point out that poly(ethylene glycol terephthalate) (PET)[23] exhibits a mechanical γ relaxation similar to that of PTCT, and this suggests that a common mechanism is the cause of this relaxation in PET and PCT polymers. It is believed that the two primary processes centered at −73 and −95 °C are associated with the gauche and trans conformations of the methylene bonds, respectively.[22] Accordingly, the possibility that the relaxation is caused by flip-flop motions of the rigid cyclohexane chair as it seems to occur in cyclohexyl polymer derivatives[24,25] should be ruled out.

The mechanical β relaxation of PCCS and the mechanical γ absorption of PCCT appear at roughly the same temperature, and both are symmetrical. The latter conditions suggests a single dominant relaxation mechanism involving the cyclohexane ring. The strength of the γ absorption in the cycloaromatic polyesters seems to be significantly higher than the β absorption in the cycloaliphatic ones. However, a big difference can be detected in the mechanical subglass relaxation behavior of the trans isomers of cycloaromatic and cycloaliphatic polyesters. Thus, whereas the former exhibits a symmetric peak of lower intensity than the cis,[22] the latter presents two overlapping peaks. Moreover, it is worthy to point out that the dynamic mechanical spectrum of PCT copolymers shows a γ relaxation that clearly can be resolved into two peaks, one associated with the cis structural units and the other with the trans, whereas the mechanical β absorption of the cycloaliphatic copolymer PCC only presents the contribution corresponding to the cis component. This suggests that the mechanical β relaxation in PTCS must be associated with molecular motion modes that probably involve more than two units. Hence the presence of cis structural units in the copolymer disrupts that motion, and consequently the mechanical contribution from the trans units to the β relaxation in PCC becomes negligible.

Cycloaromatic polyesters do not show a relaxation centered at −140 °C as the cis isomers of cycloaliphatic polyesters do, and this seems to indicate that the mechanical γ relaxation in the latter polymer must be caused by complex molecular motions involving skeletal bonds of the axial-substituted part of the glycol coupled with motions of some skeletal bonds of the acid residue.

The fact that the mechanical and dielectric relaxations are centered at nearly the same temperature in PCCS networks seems to suggest that the mechanisms responsible for both types of relaxations should be similar. The analysis of the structural characteristics of both PCCS and PTCS chains indicates that the molecular mechanisms that can give rise to significant dielectric activity are associated with molecular motions of the skeletal bonds of the glycol residue. The small correlation between the dipoles separated by eight methylene groups of the acid residue seems to preclude a significant contribution to the dielectric activity of the chains from motions involving these methylene groups.

Values of the square of both the dipole moment and the end-to-end distance r of the segment lying between i - 1 and $i + 7$ bonds in Figure 1 were calculated for the cis and trans isomers of PCS by substituting the cyclohexane ring for a 2.97-Å virtual bond connecting the carbon atoms in the 1,4-positions, its direction making angles $\theta_e = 149.5°$ and $\theta_a = 101.7°$ with the equatorial and axial C–H bonds,

Table III
Square Dipole Moments and Dimensions of Some Representative Conformations Corresponding to Nine Bond Segments (*i* - 1 through *i* + 7 in Figure 1) of the PCCS Chains

conformation	μ^2, D^2	r^2, Å^2
$\mathrm{ttccg^{\pm}tt}$	7.17	55.6
$\mathrm{ttg^{\pm}cg^{\pm}tt}$	7.27	115.7
$\mathrm{ttg^{\mp}cg^{\pm}tt}$	14.28	91.8
$\mathrm{tg^{\mp}g^{\pm}cg^{\pm}tt}$	1.42	120.7
$\mathrm{tg^{\pm}ccg^{\pm}tt}$	1.40	38.9
$\mathrm{ttccg^{\pm}g^{\pm}t}$	12.97	48.8
$\mathrm{tg^{\mp}g^{\pm}cg^{\mp}g^{\pm}t}$	12.75	111.2
$\mathrm{tg^{\pm}g^{\mp}cg^{\mp}g^{\pm}t}$	0.68	129.1
$\mathrm{ttccg^{\pm}g^{\pm}t}$	12.97	48.8
$\mathrm{ttg^{\pm}cg^{\mp}g^{\mp}t}$	10.73	71.2

respectively.[9] The remaining skeletal bond angles were assumed to have the following values: $\angle \mathrm{OCOCH_2} = 114°$, $\angle \mathrm{OCH_2C_yH} = 110°$, and $\angle \mathrm{CH_2COCH_2} = 113°$. Bond lengths of 1.51, 1.53, 1.33, and 1.43 Å were used for $\mathrm{CH_2{-}CO}$, $\mathrm{CyH{-}CH_2}$, O–CO, and $\mathrm{O{-}CH_2}$, respectively. Rotational states about $\mathrm{O{-}CH_2}$ bonds were assumed to be[9,10] located at ±75°. Bond rotations of the same sign about the two consecutive bonds $\mathrm{O{-}CH_2}$ and $\mathrm{CH_2{-}CyH}$ in the equatorially substituted side are not permitted; however, bond rotations of different sign are allowed and apparently have the same energy as the tt conformations. Finally, $\mathrm{CyH{-}CH_2}$ bonds in the axially substituted part are restricted to ±120°, while the rotational angles about these bonds in the equatorially substituted side are 0 and ±120°. The dipole moment associated with each ester group has a value of 1.89 D, and its direction makes an angle of 123° to the direction of the $\mathrm{CH_2{-}CO}$ bond.[26]

Taken as reference the planar conformations in Figure 1 for PTCS and PCCS are ttctctt and ttccctt, respectively, the transformation of coordinates from reference frame $i + 5$ to $i + 4$ and from $i + 3$ to $i + 2$ requires that 180° be added to the rotational angles indicated above for $i + 4$ and $i + 2$; $\theta = 0°$ and 180° for $i + 3$ virtual bond for the trans and cis isomers, respectively.

Values of μ^2 and r^2 for the conformations allowed to the cis glycol residue are shown in the second and third columns of Table III. It can be seen that the polarities corresponding to the two conformations of lowest energy ($\mathrm{ttg^{\pm}cg^{\pm}tt}$ and $\mathrm{ttg^{\pm}cg^{\pm}tt}$)[9] differ considerably, but the square of the distance is similar in both cases. Thus the values of μ^2 and r^2 are 7.27 D^2 and 115.7 Å^2 in the former conformation and 14.28 D^2 and 91.8 Å^2 in the latter. The results of Table III indicate that it is possible to postulate molecular motions involving conformational changes that entail a significant dielectric and mechanical activity. For example, transitions from $\mathrm{tg^{\pm}ccg^{\pm}tt}$ to $\mathrm{tg^{\pm}g^{\mp}cg^{\pm}g^{\mp}t}$ change μ^2 and r^2 from 1.40 D^2 and 38.9 Å^2 to 12.75 D^2 and 111.2 Å^2. It is expected that the conformational transitions that give rise to significant changes in polarity and length intervene in the β relaxation, whereas in the γ relaxation will probably take part conformational transitions in which the changes in μ^2 and r^2 are moderate. Although it is not possible to state which of the conformations in Table III will intervene in the β and γ processes, the results suggest that at least the dielectric absorptions must be caused by conformation changes that take place in the glycol residue.

The results obtained for μ^2 and r^2 in the trans glycol residue are shown in Table IV. As in the cis isomer the two conformations of lowest energy[9,10] $\mathrm{ttg^{\pm}tg^{\pm}tt}$ and $\mathrm{ttg^{\pm}tg^{\mp}tt}$ exhibit similar vlaues for r^2 (125.4 and 149.3 Å^2, respectively), but their polarities vastly differ. Thus the values of μ^2 are 7.01 and 0 D^2 for the former and latter conformations, respectively. A close inspection of the results of Table IV indicates that it is possible to postulate conformational transitions that give rise to large dielectric activity. However, the changes in r^2 are relatively small, and this suggests that the mechanical response may be caused by molecular motions in which take part conformational changes that involve skeletal bonds beyond those of the glycol residue.

Table IV
Square Dipole Moments and Dimensions of Some Representative Conformations Corresponding to Nine Bond Segments (*i* - 1 through *i* + 7 in Figure 1) of the PTCS Chains

conformation	μ^2, D^2	r^2, Å^2
ttctctt	0	123.0
$\mathrm{ttg^{\pm}tg^{\pm}tt}$	7.01	125.4
$\mathrm{ttg^{\pm}tg^{\mp}tt}$	0	149.3
$\mathrm{tg^{\pm}g^{\mp}tg^{\mp}tt}$	12.84	120.3
$\mathrm{tg^{\mp}g^{\pm}tcg^{\pm}t}$	10.71	85.5
$\mathrm{tg^{\pm}g^{\mp}tcg^{\pm}t}$	0.20	75.3
$\mathrm{ttctg^{\mp}g^{\pm}t}$	4.82	95.4
$\mathrm{tg^{\pm}g^{\mp}tg^{\mp}g^{\pm}t}$	12.07	119.4
$\mathrm{tg^{\pm}ctcg^{\mp}t}$	0	101.6
$\mathrm{tg^{\mp}ctcg^{\mp}t}$	9.16	95.8

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Registry No. (Sebacic acid)(2,4-bis(*p*-isocyanatobenzyl)phenyl isocyanate)(*cis*-1,4-cyclohexanedimethanol) (copolymer), 114532-83-1; (sebacic acid)(2,4-bis(*p*-isocyanatobenzyl)phenyl isocyanate)(*trans*-1,4-cyclohexanedimethanol) (copolymer), 114532-84-2; (sebacic acid)(2,4-bis(*p*-isocyanatobenzyl)phenyl isocyanate)(*cis*-1,4-cyclohexanedimethanol)(*trans*-1,4-cyclohexanedimethanol) (copolymer), 114532-85-3.

References and Notes

(1) Pochan, J. M.; Hinman, D. F. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 1365.
(2) Ito, M.; Nakatani, S.; Gokan, A.; Tanaka, K. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 605.
(3) Ito, M.; Kubo, M.; Tsuruta, A.; Tanaka, K. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 1435.
(4) Boyd, R. H.; Hasan, A. A. *Polymer* **1984**, *25*, 347.
(5) Boyd, R. H.; Alwyn, P. A. *Polymer* **1984**, *25*, 340.
(6) Boyd, R. H.; Alwyn, P. A. *Polymer* **1984**, *25*, 330.
(7) Alwyn, P. A.; Boyd, R. H. *Polymer* **1984**, *25*, 323.
(8) Boyd, R. H. *Polymer* **1985**, *26*, 323.
(9) Riande, E.; Guzmân, J.; de la Campa, J. G.; de Abajo, J. *Macromolecules* **1985**, *18*, 1583.
(10) Riande, E.; Guzmân, J. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *18*, 1553.
(11) Riande, E.; Guzmân, J.; Mark, J. E. *Polym. Eng. Sci.* **1986**, *26*, 297.
(12) Guzmân, J.; de Abajo, J.; Pereña, J. M.; Riande E., unpublished results.
(13) McCrum, N. G.; Read, B. E.; Williams, G. *Anelastic and Dielectric Effects in Polymeric Solids*; Wiley: New York, 1967. Boyd, R. H. *Polymer* **1985**, *26*, 1123.
(14) Porter, C. H.; Boyd, R. H. *Macromolecules* **1971**, *4*, 589.
(15) Williams, G. *Adv. Polym. Sci.* **1979**, *33*, 59.
(16) Doolittle, A. K.; Doolittle, D. B. *J. Appl. Phys.* **1957**, *28*, 901.
(17) Williams, M. L.; Landel, R. F.; Ferry, J. D. *J. Am. Chem. Soc.* **1955**, *77*, 3701.
(18) Plazek, J. D.; O'Rourke, V. M. *J. Polym. Sci., Polym. Phys. Ed.* **1971**, *9*, 208.
(19) Ferry, J. D. *Viscoelastic Properties of Polymers*; Interscience: New York, 1981.
(20) Tonelli, A. E. *J. Chem. Phys.* **1970**, *52*, 4749.
(21) Riande, E. *Macromol. Chem., Macromol. Symp.* **1986**, *2*, 179.
(22) Hiltner, A.; Baer, E. *J. Macromol. Sci., Phys.* **1972**, *B6*, 545.
(23) Illers, K. H.; Breuer, H. *J. Colloid Sci.* **1963**, *18*, 1.
(24) Heijboer, J. Doctoral Thesis, Leiden, 1972.
(25) Heijboer, J. *Molecular Basis of Transitions and Relaxations*; 1984; p 277.
(26) Saiz, E.; Hummel, P. J.; Flory, P. J.; Plavsic, M. *J. Phys. Chem.* **1981**, *85*, 3211.