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Dielectric Studies of Various Olefin/SO_2 Copolymers

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Dielectric constant and loss have been measured at low and high frequencies for several poly(1-olefin sulfones) as well as for the polysulfones of allybenzene and allyl cyclopentane. The low-frequency dispersion in allylbenzene due to helical sequences is weaker in benzene than in dioxane, and in both solvents is much lower than for the 1-olefin polymers. Solvent effects on the high frequency process are also reported, but yield no simple uniform picture.

Introduction

It has been recognized for some time that the low-frequency molecular-weight dependent dielectric dispersion observed[1] in solutions of 1-olefin/sulfur dioxide alternating copolymers is due to the presence of helical sequences[2,3], and in fact such helices have been directly observed by transmission electron microscopy[4]. There is also a second, higher frequency process independent of molecular weight, that has been attributed either to the existence of more or less randomly coiled sequences[5] or to rotation about their long axes of the helical sequences.[6,7]

In the present paper we offer some additional observations on such systems. Data are reported for two copolymers not previously studied, poly(allylbenzene) sulfone and poly(allylcyclopentane)sulfone, and solvent effects are measured for several other copolymers at both low (0.2 kHz) and high (2 MHz) frequencies. Somewhat surprisingly, there is considerable difference in the magnitude of the response between the allylbenzene and allylcyclopentene copolymers. The terpolymer method of Fawcett and Fee[2] is applied to systems containing allylbenzene and 1-eicosene with cyclohexene and SO_2.

Experimental

Cyclohexene, 1-hexene, 1-dodecene, 1-eicosene, allylcyclopentane and allylbenzene were obtained from Aldrich Chemical Co. and were distilled prior to use. Sulfur dioxide was from a Matheson lecture bottle. Benzene, dioxane and toluene were purified by refluxing over sodium under nitrogen for about 30 hrs. and subsequently distilling under nitrogen. Carbon tetrachloride was purified by refluxing over P_2O_5 and subsequently distilling under nitrogen.

Polymerizations were effected by the free-radical mechanism, with *t*-butyl hydroperoxide (Aldrich) in toluene or 2,2,4-trimethylpentane as initiator. The monomers, initiator and SO_2 were condensed at dry ice temperature and then warmed to 0° C or the boiling point. After about 3 hrs. the obtained polymer was dissolved in chloroform and precipitated in 2 L of methanol slightly acidified by HCl to promote coagulation. The polymer was filtered the next day, washed with methanol at least 4 times and finally dried in a vacuum oven overnight. Conversions were over 70% in all cases.

The polymer compositions and structures were confirmed by elemental analyses, UV absorption, IR and ^{13}C NMR spectra. The molar compositions of the terpolymers with cyclohexene and 1-eicosene were calculated from elemental anayses, while those of cyclohexene and allylbenzene were based on 300 MHz proton spectra.

Poly(allylbenzene)sulfone (PABS) was divided into six fractions, with benzene as solvent and methanol as non-solvent. Molecular weights were determined with a Brice-Phoenix ligh-scattering photometer and differential refractometer, and intrinsic viscosities in chloroform and dioxane were measured at 30° C with Ubbelohde viscometers. The resulting Mark-Houwink-Sakurada relations are:

$$[\eta] = 1.14 \times 10^{-4} M^{0.66} dL/g \text{ in chloroform}$$

and

$$[\eta] = 2.50 \times 10^{-4} M^{0.63} dL/g \text{ in dioxane.}$$

Rough extrapolation of these results gives a characteristic ratio C_∞ of about 7.5.

The dielectric response of the polysulfones in various solvents was measured at Dartmouth over the frequency range 100 Hz to 150 kHz, with a General Radio Type 1620-A capacitance and loss measuring assembly, supplemented by a General Radio 1330-A oscillator and Hewlett-Packard 3300A Function Generator. Some of the measurements were carried out in a Balsbaugh Laboratory Model 350-G three-terminal cell in a brass jacket with a tight Teflon cover. For smaller samples we used a home-built stainless steel cell that has been described elsewhere.[8] The temperature was maintained at $30.00 \mp 0.02°$ C during the measurements. The contributions of ionic conductivity to the permittivity at low frequencies were eliminated when possible by extrapolating $e'f^2$ or $e''f$ against f^2, as in previous contributions from the Dartmouth laboratory[9].

Data at 2 MHz were obtained at the Technical University of Istanbul with a WTW 01 Dipolmeter made by Wissenschaftlich Technische Werkstätten GmbH in a DFL1-Type cell. For PABS and poly(allylcyclopentane)sulfone measurements in the range 1 to 100 MHz were performed at Brown University by the time domain reflectometry technique, thanks to the kind hospitality and help of the late Professor R. H. Cole and Dr. Paul Winsor IV.

Results and Discussion

An example of the dielectric increment and loss factor displaying both low and high frequency dispersion regions is shown in Figs. 1 and 2 for poly(allylbenzene)sulfone (PABS) in the solvents benzene and dioxane. The two regions are well separated, with an intermediate plateau value near 1 MHz. Thus we can clearly separate the two contributions to the dielectric increment, writing, as previously,[9]

$$\langle\mu_p^2\rangle/r = \frac{27k_BTM_o}{4\pi N_A d_1}\left[\frac{(\Delta\epsilon_o/w)-(\Delta\epsilon_u/w)}{(\epsilon_1+2)^2}\right] \tag{1}$$

$$\langle\mu_s^2\rangle/r = \frac{27k_BTM_o}{4\pi N_A d_1}\left[\frac{(\Delta\epsilon_u/w)}{(\epsilon_1+2)^2}-\frac{2n_1(dn/dw)}{(n_1^2+2)^2}\right] \tag{2}$$

where M_o is the molar mass of a repeat unit; N_A is Avogadro's number; d_1, ϵ_1 and n_1 are density, dielectric constant and refractive index of the pure solvent; $\Delta\epsilon_o$ is the limiting low-frequency permittivity; $\Delta\epsilon_u$ is the intermediate plateau value; (dn/dw) is the refractive index increment; r is the degree of polymerization; w is the weight fraction of solute; and μ_p and μ_s represent contributions to the molecular dipole moment parallel and perpendicular to the chain axis. The brackets denote average values. The low-frequency relaxation is, as already mentioned, due to the existence of helical sections.

Applying Eq. (1) to the data for PABS, we obtain a value of about 1.2 D^2 for the low-frequency process in dioxane, with a slight dependence on molar mass (parallel dipoles in a good solvent), while the comparable figure in benzene is 0.72 D^2. The high-frequency contribution, from Eq. (2), amounts to 3.8 D^2 in dioxane and 0.85 D^2 in benzene. The low-frequency results are distinctly different from those for poly(1-hexene sulfone)[5]; the values of both permittivity and loss are many times smaller in PABS than in the 1-hexene polymer; and in PABS the values of ϵ' in both dispersion regions are larger in dioxane, while in poly(1-hexene sulfone) the low-frequency figures in benzene are three times as large as those in dioxane.

The relaxation times for the low frequency process are in rough agreement with the relation

$$\tau \cong M[\eta]\eta_o/RT, \tag{3}$$

where η_o is solvent viscosity, and works well for other polysulfones[1,5]. According to this relation, the process is slower in dioxane, which has the greater viscosity, as is seen in Figs. 1 and 2. However, the high frequency process is faster in dioxane, as was also true for poly(1-hexene sulfone)[5]. Thus the effects of solvent on both magnitude and rate are not easily rationalized.

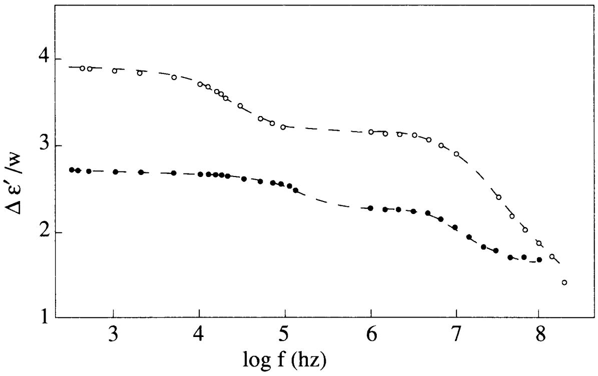

Figure 1. Permittivity of poly(allylbenzene sulfone) in dioxane (open circles) and benzene (filled circles) at ca. 3% w/w concentration at 30°C. Molar masses are 10^5 g/mol for the lower region of dispersion and 4×10^4 g/mol for the higher region.

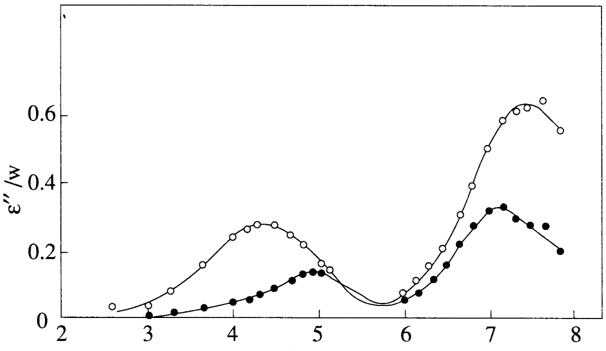

Figure 2. Dielectric loss factor of same solutions as in Fig 1.

A few other low-frequency permittivity data are shown in Table 1, almost entirely at the single frequency 0.2 kHz, which for the molar masses involved are close to the limiting low-frequency plateau values $\Delta\epsilon_o$. In Table 2 we give a number of observations at the sinle frequency 2 MHz, which falls in all cases in the range of the intermediate plateau value $\Delta\epsilon_u$. From these two tables we can then compute values of $\langle\mu_p^2\rangle$ /r and $\langle\mu_s^2\rangle$ /r according to Eqs. (1) and (2), and these are displayed in Table 3, where we have also included the figures for PABS quoted previously and based on Figs. 1 and 2.

Table 1. Low Frequency (0.2 kHz) Dielectric Increments for Various Poly(1-olefin sulfones) at 25 °C

Olefin	Solvent	$(\Delta\epsilon_o/w)$
1-hexene	benzene[a]	14.1
	dioxane[a]	8.34
	CCl_4	25.5
1-dodecene	benzene	14.6
	CCl_4	34.7
1-eicosene	benzene	11.0
allylcyclopentane	dioxane	7.30
cyclohexene	benzene	2.20
	dioxane	2.55

[a] See ref.5.

Table 2. Dielectric Increments at 2 MHz for Various Polymers at 25 °C

Olefin	Solvent	$(\Delta\epsilon_u/w)$	$d\ln\langle\mu^2\rangle/dT \times 10^3$ (K^{-1})
1-butene	dioxane	4.28	
1-hexene	toluene	3.14	5.0
	benzene	3.41	5.2
	CCl_4	4.03	1.2
	dioxane	4.48	2.5
1-dodecene	benzene	1.57	
	dioxane	2.24	
	CCl_4	1.83	
1-eicosene	benzene	0.89	
allylcyclopentane	dioxane	4.39	
cyclohexene	benzene	2.17	1.1
	dioxane	2.99	-1.9
	toluene	2.47	-4.7

In Table 3 we observe that the values for $\langle\mu_p^2\rangle$ /r are somewhat higher for the 1-dodecene and 1-eicosene polysulfones than for poly(1,hexene sulfone). This trend agrees with that observed earlier and justified theoretically.[10] In contrast, the figure for poly(allylcyclopentane sulfone) in dioxane is almost identical to that for the 1-hexene polymer, while that for poly(allylbenzene sulfone), as already remarked, is much lower. Thus the reduced helical contribution in the latter polymer cannot be attributed to a broader side group, and must somehow be related to the aromatic ring in allylbenzene. For poly(cyclohexene sulfone), with symmetry about the double bond, the low frequency contribution essentially vanishes.[7] The table contains the first results reported for carbon tetrachloride, which is seen to favor the helical contribution strongly. For $\langle \mu_s^2 \rangle / r$ we see that in general the figures for dioxane are greater than those in benzene or CCI_4. It should also be emphasized that for the two known examples, 1-hexene[5] and now allylbenzene, the relaxation frequency is higher in dioxane than in benzene, though the former solvent is twice as viscous as the latter. This would seem to mitigate against the suggestion[6,7] that the high-frequency process involves a rotation of helical sections about the helical axis, but would not be inconsistent with segmental rearrangements in random-coil sections with different local structures in the two solvents. A third possibility, that of helix-to-coil sections with different local structures in the tjo solvents. A third possibility, that of helix-to-coil conversions at the termini of the sequences, is also possible, though the theory for this situation seems hard to construct. The details of such local processes are likely to involve more than one type of motion[11]. We also point out that the few values for the temperature coefficient in the last column of Table 2 show a diversity in their dependence on solvent.

It remains for us to describe the measurements of the low-frequency process in the terpolymers involving 1-eicosene and allylbenzene with cyclohexene and SO_2. The results are shown in Figs. 3 and 4, where the ordinate gives values of $\langle \mu_p^2 \rangle$ relative to that in the copolymer containing no cyclohexene, and the abscissa x gives the mole fraction of l-eicosene or allylbenzene in the olefin content of the polymer. To discuss these results guantitatively, we employ the simplest model of Fawcett and Fee[2], in which each repeat unit has an independent probability of joining in a helical sequence and no account is taken of end effects.

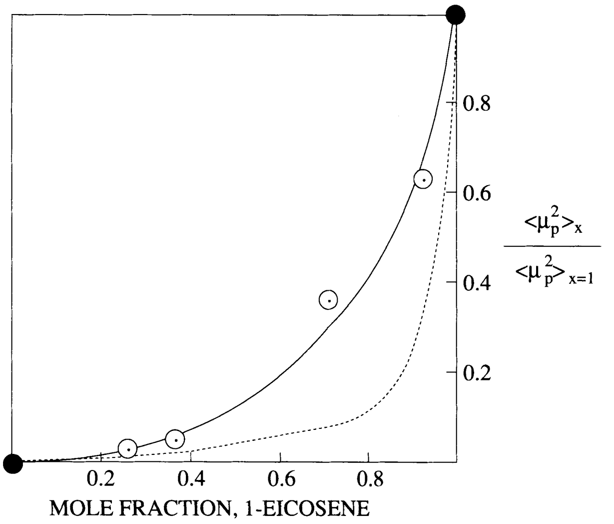

Figure 3. Reduced parallel (helical) dipole moments in benzene at 25° C of terpolymers containing 1-eicosene (x), cyclohexene (1-x) and SO_2.

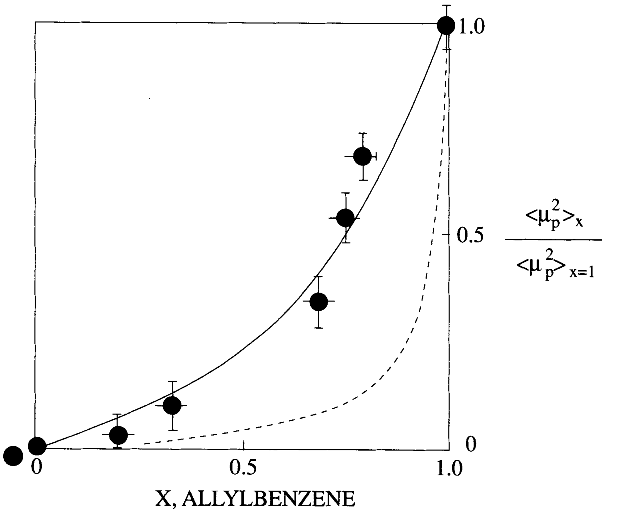

Figure 4. Reduced parallel (helical) dipole moments in benzene at 30° C of terpolymers containing allylbenzene (x), cyclohexene (1-x) and SO_2.

This model gives

$$\langle \mu_p^2 \rangle_x / \langle \mu_p^2 \rangle_{x=1} = x(1-p)(1+px)/(1+p)(1-px), \tag{4}$$

where p is the probability of a helical placement in the copolymer (x=1). From Fig.3 we find p=0.85 for

1-eicosene, and Fig. 4 yields p=0.58 for allylbenzene. In contrast, the dotted curve for 1-hexene, shown in both Eqs. 3 and 4 and obtained earlier by Fawcett and Fee[2], gives p=0.95. These results are all for benzene as the solvent.

Table 3. Low Frequency (Helical) and High Frequency Dipole Contributions

Olefin	Solvent	$\langle\mu_p^2\rangle$/r (D^2)	$\langle\mu_p^2\rangle$/r(D^2)
1-butene	dioxane	a	3.80
1-hexene	benzene	18.8	4.5
	dioxane	9.5	5.0
	CCI_4	19.4	2.9
1-dodecene	benzene	31.1	3.3
	CCI_4	41.5	1.9
1-eicosene	benzene	32.0	
allylcyclopentane	dioxane	9.7	5.6
allylbenzene	dioxane	1.2	3.8
	benzene	0.72	0.85
cyclohexene	benzene	0	2.66
	dioxane	0	3.03
	toluene	–	2.96

[a] See ref.7

According to this model, the weight-average length of a helical segment in the copolymer containinig no cyclohexene is just

$$\langle m\rangle_w = (1+p)/(1-p), \tag{5}$$

which yields figures of 12.3, 3.8 and 39 for the three polymers in the order given above. Clearly, the value for allylbenzene is too small to be taken seriously, since the preferred helix model[10] requires about 5 units per single turn.

Going one step further, we may write (again without cyclohexene)

$$\langle\mu_p^2\rangle/r = \mu_R^2 p(1+p)/(1-p), \tag{6}$$

where μ_R is the projection of a repeat-unit dipole along the helical axis. Then from we obtain μ_R=1.75 D, 0.74 D and 0.71 D for 1-eicosene, allylbenzene and 1-hexene polymers, respectively. The figure for 1-eicosene seems anomalously high, but the other two are surprisingly close to the values, ranging from 0.55 D to 1.1 D, estimated by Mansfield[10] from conformational energy calculations. If we assume a value of μ_R=0.75 D for the 1-dodecene polymer, we find from Eq. (5) that p=0.97 similar to the Fawcett-Fee[2] result for the 1-hexene polymer. To bring the 1-eicosene result into line with these, an inordinately large error in the terpolymer measurements would have to be assumed. Indeed, if the single point in Fig. 3 at $x=0.7$ were to be reduced by 20%, the eicosene values would change to $p=0.89$ and $\langle m \rangle_w=17$, somewhat closer to those for the other 1-olefins.

We should also mention that the conformational details in these polymers are certainly more complex than we have managed to treat here, especially since liquid-crystalline behavior has been detected[12] in the sulfones of 1-hexadecene and 1-eicosene as well as some terpolymers of these with cyclohexene.

Acknowledgments

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