Bisphenol-A Polycarbonate Immersed in Organic Media. Swelling and Response to Stress

R. P. Kambour,* C. L. Gruner,[1] and E. E. Romagosa[1]

Research and Development Center, General Electric Co., Schenectady, New York 12301. *Received November 5, 1973*

ABSTRACT: The degree of swelling and attendant T_g reduction have been determined for bisphenol-A polycarbonate in a wide spectrum of organic small-molecule agents. Critical strains for craze initiation have been determined in the same agents. Swelling and crazing profiles are similar to those previously found for polysulfone. Crazing resistance is best correlated by the degree to which plasticization reduces T_g toward ambient temperature. Critical strain in air is greater the greater is the interval ΔT between T_g and the test temperature. A second factor intrinsic to the polymer controls the proportionality constant k between ϵ_c and ΔT; the value of k for polycarbonate is the same as for polysulfone but three times the value of k for polystyrene and poly(phenylene oxide). This difference in k's is discussed in terms of secondary relaxations in moduli and their implications for homogeneous creep at higher temperatures.

Previous reports from this laboratory have detailed the results of extensive studies of the swelling of three glassy polymers over a wide range of organic liquids, of the attendant reductions in their T_g's and of the reductions in their resistance to craze initiation. These polymers—poly(phenylene oxide),[2a] polysulfone,[2b] and polystyrene[3] have differed substantially each from the other in at least one important characteristic (see Table I).[2-8]

The results of these studies are summarized as follows. (1) **Swelling.** The degree of swelling of each polymer by a given liquid tends to be correlated by solubility parameters of polymer δ_p and liquid δ_s. However, specific interactions like hydrogen bonding as well as molecular size and shape limit this correlation. In addition the excess free energy of the glassy state increases susceptibility of all these materials to limited degrees of swelling across the entire spectrum of liquids. Finally, for unknown reasons the general size of the swelling envelope (degree of swelling *vs.* δ_s) varies from polymer to polymer. (2) **T_g reduction.** Whatever the degree of swelling the depressed T_g of the polymer is correlated roughly by the Kelley-Bueche equation.[9] (3) **Crazing Resistance.** The reduction in T_g serves to correlate the reduction in critical strain for craze initiation ϵ_c down to a T_g not far above ambient temperature and to a threshold of strain that is approximately 0.1–0.2%. Further reductions of T_g by increased swelling are ineffective in lowering resistance to craze or crack initiation. In fact, at very high levels of swelling ϵ_c is often seen to increase again as other modes of stress relaxation become much more important than crazing. (4) **Auxiliary experiments,** in which controlled amounts of dichlorobenzene were mixed with polystyrene and molded into bars that were subsequently tested for crazing resistance in air, have shown that the correlation of ϵ_c *vs.* T_g is identical within experimental error to that obtained from the aforementioned polystyrene solvent crazing tests.[3]

On the basis of these results we believe that the key role (or roles) of organic agents in the mechanism of solvent crazing is entirely connected with flow processes in the glassy state. In short, organic agents dissolve in polymers and act as plasticizers. Conversely, organic agents have no measurable effect as surface stabilizers, contrary to the hypotheses of other workers.

A study elsewhere[10] of the solvent crazing resistance of poly(methyl methacrylate) and poly(vinyl chloride) is consistent, as far as it goes, with the findings discussed above.

I. Characteristics of Bisphenol-A (BPA) Polycarbonate

The subject polymer of this study most closely resembles polysulfone of the three materials previously characterized (Table I). Both materials have high T_g's, ductility in Instron tensile tests, and sizable low-temperature modulus dispersions. Their chemical structures have in common the BPA residue and their solubility parameters are relatively high for glassy thermoplastics. They differ substantially in one respect. Polycarbonate can develop 20% crystallinity when its T_g is lowered below ambient temperature by swelling while polysulfone is totally amorphous under all conditions.[11]

In this connection Miller, Visser, and Morecroft[12] have postulated that stresses generated by swelling-induced crystallization are responsible for solvent crazing-cracking of polycarbonate. While the dimensional changes occurring as a result of crystallization may cause the generation of internal stresses, these are obviously not responsible for crazing when the degree of swelling is not sufficient to lower T_g below ambient. Moreover, the solvent crazing and cracking of poly(phenylene oxide), which also can be crystallized as a result of swelling, show no special enhancement in liquids causing crystallization.

The present study serves to characterize the swelling and crazing behavior of polycarbonate and to compare this material with polysulfone. The similarity of the results for these two materials serves to reinforce our belief that swelling-induced crystallization exerts little influence on polycarbonate crazing behavior under most circumstances.

II. Experimental Section

As in previous studies the liquids used ranged in solubility parameter from that of dodecamethylpentasiloxane (5.34) to that of formamide (19.2) and water (25.0). In order to explore the effects of molecular size this study was expanded to encompass linear aliphatic hydrocarbons and monohydric alcohols of chain lengths up to 16 and 12 carbons, respectively. (Two alcohols of greater molecular weight were also used but these were branched.) All liquids used were reagent grade except for a few of the alcohols, as noted in Table II.

Critical strains for craze initiation were determined for bars cut from sheets compression molded at 220–230° from dried pellets of Lexan (General Electric Co.) 131 bisphenol-A polycarbonate ($[\eta]_0$ = 0.67 dl/g). These measurements were made using Bergen elliptical strain jigs in the manner previously described.[2b] Each test involved strapping the specimen to the jig and then contacting the bar surface with the respective test liquid. In some liquids contact was effected by immersion of the whole jig assembly. With other liquids, particularly those that tended to cause cracks from the specimen edges, narrow wicks were laid on the center line of the specimen and wetted carefully using a syringe; in this way the specimen edges remained dry.[2b] At least two bars were tested for each liquid. With several liquids duplicate sets of measurements were made at a later time from newly molded sheets.

Table I

Polymer	DSC T_g (°C)	Solubility Parameter (cal/cm^3)$^{1/2}$	Crystallizability	Low-Speed Tensile Failure	Low-Temp Modulus Relaxation
Poly(2,6-dimethyl-1,4-phenylene oxide)	213[2a]	8.6[2a]	~15[2a]	Ductile	Small–medium[5]
Polysulfone	186[2b]	10.8[2b]	0[2b]	Ductile	Large[6]
Polystyrene	104[3]	8.8[3]	0	Brittle	Very small[7]
Polycarbonate	159	9.8	~20[4]	Ductile	Large[6,8]

Average values of ϵ_c for each set of measurements are reported here.

Swelling measurements were carried out as previously described using pieces of 0.001-in. thick extruded Lexan 100 polycarbonate film ($[\eta_0]$ = 0.58 dl/g). Films were exposed to saturated vapor at ambient temperature (23–24°) and removed intermittently for weighing over a period of 319 days—a time great enough for equilibrium to be achieved in every case. Subsequently, the T_g's of many of these swollen films were detected with a Perkin-Elmer DSC IB scanning calorimeter run at a scanning rate of 20°/min. Swelling-induced crystallinity was detectable, when present, by the appearance of melting endotherms in the calorimeter traces.

III. Results

All experimental results together with the solubility parameters, densities, and T_g's (where known) of the liquids used are listed in Table II. In each of these cases the smaller value of critical strain has been used in the critical strain correlations shown in Figures 3 and 4.

In several cases marked discrepancies are evident in the duplicate values of ϵ_c. These discrepancies are believed to have arisen from variations in degree and/or direction of orientation in the molded bars.[13] On this basis we believe that in each case the smaller of the duplicate values of ϵ_c listed in Table I is closer to the true value of ϵ_c for completely isotropic polymer.

Swelling. The solubility of diluent in the polymer S_v (volume of liquid absorbed at equilibrium per unit volume of polymer in the amorphous state) is plotted *vs.* liquid solubility parameter δ_s in Figure 1. An envelope is drawn through the outermost data. A similar swelling envelope which had been drawn through the outermost swelling data for polysulfone is also shown for comparison. The envelopes for the two polymers are similar in shape, magnitude, and position on the δ_s scale—particularly below S_v = 0.25.

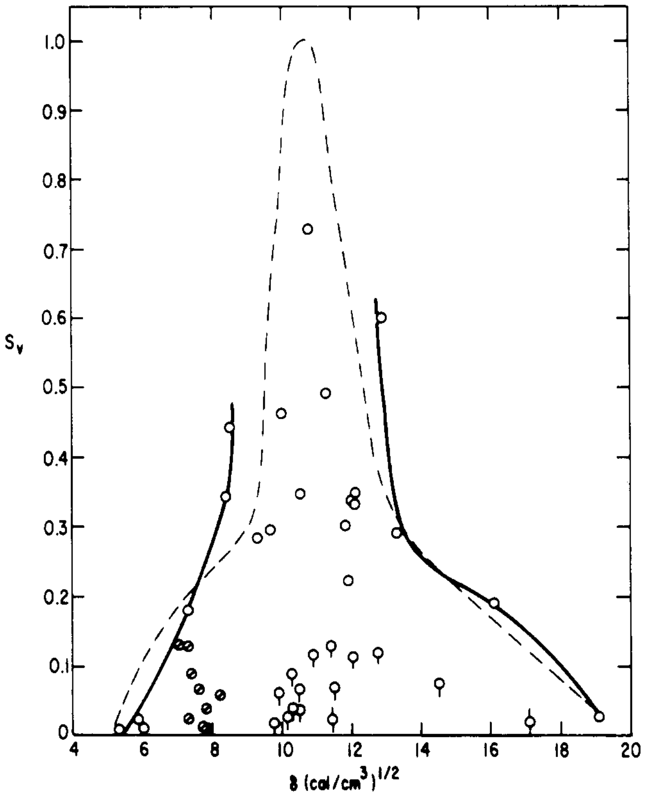

Figure 1. Volume solubility S_v of saturated vapors in polymer *vs.* δ. Solid line is swelling envelope drawn to reflect uppermost points. Broken line is envelope for polysulfone from ref 2b. Single tab, monohydric alcohol; double tab, dihydric alcohol; slanted bar, aliphatic hydrocarbon.

As with polysulfone, polystyrene, and poly(phenylene oxide) the polycarbonate envelope has a base broad enough to span the entire range of organic liquid solubility parameters. The envelope also has an upper, narrower section as is the case with the other polymers. All liquids of this study that swell the polymer to greater than 20 vol % induce polymer crystallization. This crystallization constitutes the simplest and most direct evidence of the fact that 20% swelling is enough to reduce polymer T_g below ambient temperature. Thus, as with the three other polymers, the broad base joins the narrower portion of the envelope where S_v is sufficient to reduce T_g to ambient. The existence of the broad base is again believed to result from the fact that the excess free energy of the polymeric glassy state provides an additional driving force for swelling not present in the (equilibrium) liquid state of the polymer.

As with polysulfone all aliphatic alcohols are much less soluble than other liquids having corresponding values of δ_s. With both polymers this behavior is thought to result from the widely understood inadequacy of the Scatchard–Hildebrand theory[15] of solubility in calculating the heats of interaction of different molecular species when one or both of these are hydrogen bonded or strongly polar. In neither polymer are groups present in high concentration that are as strong hydrogen-bonding bases as are the oxygens in aliphatic alcohols. Consequently, the heats of interaction of alcohols with these polymers are believed to be lower than predicted by the Scatchard–Hildebrand geometric mean assumption and thus solubility is lower than with other liquids.

The solubility of linear aliphatic hydrocarbons decreases rapidly with chain length above five or six carbons. The same is true for linear monohydric alcohols above pentanol. Less extensive swelling data for these two classes of liquids in polysulfone and polystyrene showed similar trends. With poly(phenylene oxide), S_v's of the linear alkanes increase with molecular length up to eight carbons but apparently decrease above this length. In all these cases the decreases in S_v with chain length occur in spite of increasingly favorable solubility parameters. The source of the decreases is undoubtedly the change in the configurational entropy of swelling with molecular length but no formal treatment of these effects has yet been elaborated.

The swelling envelope above S_v = 0.2 is broader than that drawn for polysulfone. This difference may be more apparent than real, however. The two liquids at the up-

Table II

Compounds	δ_s[d] (cal/cm^3)$^{1/2}$	ρ_s[d] (g/cm^3)	$S_v \times 10^2$ (cm^3/cm^3)	$T_{g,s}$ (°K)	T_g (°C)	ϵ_c (%)
Dodecamethylpentasiloxane	5.35	0.88	0.84		127	1.19, 1.78
Perfluoromethylcyclohexane	5.85	1.788	~2.0		146	1.59
Hexamethyldisiloxane	6.0	0.762	0.81		135	1.48, 1.66
n-Pentane	7.05	0.626	12.9	64[a]	78	0.83, 1.09
n-Hexane	7.3	0.660	12.9	70[a]	86	0.95, 1.08
2,3-Dimethylpentane	7.3		~2.1	~83[c]	121	0.97, 1.10
$C_2F_3Cl_3$ (Freon 113)	7.3	1.358	18.0		143	0.95, 1.26
n-Heptane	7.4	0.684	8.62	84[a]	95	0.94, 1.02
n-Octane	7.6	0.703	6.5	85[a]	106	0.82, 1.03
n-Decane	7.7	0.730	0.8			1.05
Methylcyclohexane	7.8	0.769	3.6	85[e]	125	0.81, 0.92
n-Hexadecane	7.84	0.775	0.3			1.27
n-Tetradecane	7.85	0.765	1.14			1.18
Cyclohexane	8.2	0.779	5.4	80[e]	83	0.84, 0.88
Isoamyl butyrate	~8.4 (calcd)		34.0		52	0.18
n-Butyl acetate	8.5	0.883	44.2		21	0.36, 0.38
Carbon tetrachloride	8.6					0.46
Methyl *n*-propyl ketone	8.7					0.53
Methyl *n*-butyrate	8.9					0.50
Methyl ethyl ketone	9.3	0.805	28.4		59	0.14, 0.50
Tridecanol (branched)	9.6					1.04
Methyl acetate	9.6					0.39, 0.78
Acetone	9.6	0.790	29.7		54	0.44, 0.57
1-Dodecanol	9.8		1.6			1.17
Undecanol (branched)	9.9	0.833	6.3			1.02
Nitrobenzene	10.0	1.20	46.2		−12.5	0.51, 0.51
1-Decanol (tech)	10.1	0.829	2.5			0.97
1-Nonanol (tech)	10.3	0.827	8.7			1.15
1-Octanol	10.3	0.825	3.9			0.93
Heptanol (branched)	10.5	0.822	3.3			0.72
3-Butenenitrile	10.5	0.832	6.5			
Cyclopentanone	10.5	0.949	34.7			
N,N-Dimethylacetamide	10.8	0.937	72.8			
1-Pentanol	10.9	0.814	11.5	124[a]	73	0.91, 0.91
Nitroethane	11.1					0.72
Dioxolane	11.3	1.06	49.3			
1-Butanol	11.4	0.810	12.7	118[a]		0.94
Cyclohexanol	11.4					0.98
Triethylene glycol	11.4	1.125	2.0		129	0.94, 1.02
Isopropyl alcohol	11.5	0.785	6.4	121[a]	89	1.01, 1.02
Methylene iodide	11.8	3.33	30.1			
Acetonitrile	11.9	0.786	22.2		61	0.32, 0.82
Dimethyl sulfoxide	12.0	1.10	33.5	153[b]		0.25, 0.40
1-Propanol	12.0	0.804	11.1	109[a]	87	0.76, 1.05
N,N-Dimethylformamide	12.1	0.949	38.0		21	1.57
Benzyl alcohol	12.1	1.042	34.7		22	0.17, 0.35
Ethanol	12.7	0.789	11.8	100[a]	119	0.84, 1.02
γ-Butyrolactone	12.9	1.129	60.3			
β-Propiolactone	13.3					0.60
Propylene 1,2-carbonate	13.3	1.20	29.3			0.28
Propylene glycol	13.7	1.036		~160[c]	108	1.41, 1.51
Methanol	14.5	0.791	7.3	110[a]	102	0.98, 1.37
Ethylene carbonate (extrap ϵ_c)	14.7					0.52
N-Methylformamide	16.1	1.011	19.0		54	0.26, 0.39
Glycerol	16.5			~185[c]		0.77
Ethylene glycol	17.1	1.109	1.8		128	1.9
Formamide	19.2	1.133	2.5		131	1.30, 1.79
Water	25.0			135[b]		1.9
Dry polycarbonate in air		1.19			159	1.9

[a] J. A. Faucher and J. V. Koleske, *Phys. Chem. Glasses*, **7**, 202 (1966). [b] D. H. Rasmussen and A. P. MacKenzie, *Nature (London)*, **220**, 1315 (1968). [c] W. Kauzman, *Chem. Rev.*, **43**, 219 (1948). [d] From ref 2a except as noted. [e] M. R. Carpenter, D. B. Davies, and A. J. Matheson, *J. Chem. Phys.*, **46**, 2451 (1967).

permost end of the left-hand polycarbonate line (δ_s = 8.4 and 8.5) were not used with polysulfone; excepting these two points and that for γ-butyrolactone at δ_s = 12.9 and S_v = 0.60, all data lie inside the polysulfone envelope.

The solubility parameter δ_p calculated by Small's method for polysulfone is 10.5–10.8, consistent with the maximum in its S_v. For polycarbonate δ_p is calculated to be 9.8–10.0. Both calculations are open to some doubt in that they depend on the use of group contributions for the carbonate group and the sulfone group that are derived from data for a very limited number of small molecule, aliphatic carbonates and sulfones. In any case the two polymers appear to be so nearly alike in swelling characteristics that a limited degree of polymer–polymer solubility would not be surprising.[16]

The scatter of swelling data within the envelope above

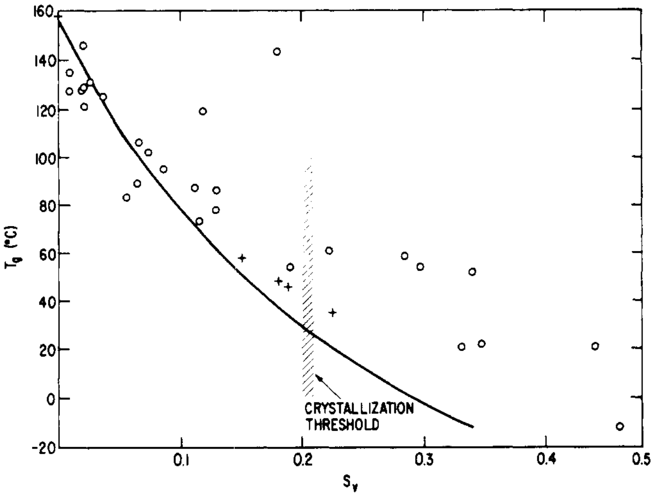

Figure 2. T_g of swollen polymer film *vs.* volume solubility S_v. Circles, data of this study; crosses, torsion pendulum loss maxima of polycarbonate swollen with acetone at various partial pressures.[4] Line is from Kelley-Bueche equation with solvent T_g = 100°K, solvent $\alpha_s = 1.2 \times 10^{-3}$ deg^{-1}, and polymer $\Delta\alpha = 3.8 \times 10^{-4}$ deg^{-1}.

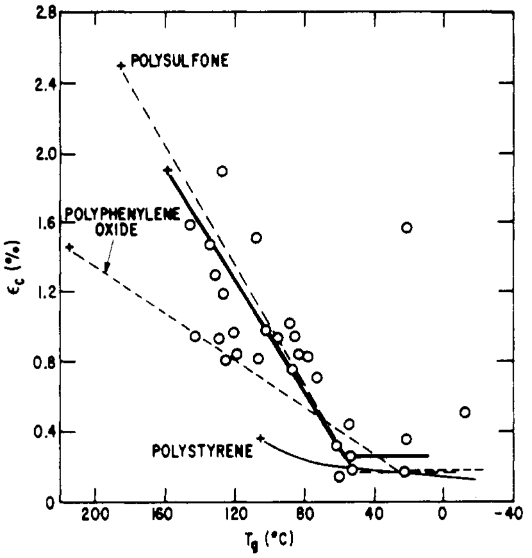

Figure 3. Critical strain ϵ_c for crazing or cracking of polymer bar *vs.* T_g of solvent-equilibrated film. Circles and heavy solid line, polycarbonate. Correlation lines for other polymers taken from previous studies.[2a,b,3]

S_v = 0.2 probably reflects the inadequacy of δ_s as a correlating parameter for polymer swelling both in polar liquids and in liquids of differing molecular shape and size. Moreover, the polymer crystallization produced by these liquids certainly reduces the solubilities substantially from what their levels would be in totally amorphous polymer. Thus, some of the swelling scatter may arise from variations from liquid to liquid in the degree of solvent rejection with occurrence of crystallization.

T_g Reduction. In Figure 2 the T_g of each swollen film is plotted *vs.* S_v. The solid line is calculated from the Kelley-Bueche equation

$$T_g = [\Delta\alpha_p T_{g,p}(1 - V_s) + \alpha_s T_{g,s} V_s]/[\Delta\alpha_p(1 - V_s) + \alpha_s V_s]$$

by setting the solvent expansion coefficient $\alpha_s = 1.2 \times 10^{-3}$, the change in polymer expansion coefficient at T_g $\Delta\alpha_p = 3.8 \times 10^{-4}$,[18] and the solvent T_g = 100°K. (The last is a value probably representative of the average T_g of the liquids used.) With the assumption of volume additivity, the volume fraction of diluent $V_s = S_v/(1 - S_v)$. With one exception agreement between line and data is remarkably good for S_v's below 0.2. Additional support for the approximate validity of these data is obtained by comparison with the T_g's of polycarbonate swollen to equilibrium at various partial pressures of acetone (crosses in Figure 2).[4,19]

Above S_v = 0.2 several of the T_g–S_v data of the current study appear to lie noticeably above not only the Kelley-Bueche line but also any reasonable extrapolation based on the acetone torsion pendulum data. All of the films involved were semicrystalline at the time of calorimetric measurements. The source of the "deviations" is not understood although possibly the crystallinity has influenced the relaxation process.

Critical Strain Reduction. In Figure 3 the critical strain ϵ_c for crazing or cracking is plotted *vs.* the corresponding swollen film T_g. Shown for comparison are the ϵ_c–T_g correlation lines for the three polymers previously studied. In every case but polystyrene the procedure has been to draw through the data a straight line pinned at the top end to the point for dry polymer. The lower end of each line was located at a point below which further T_g reduction brings no further lowering in ϵ_c. The polystyrene line is that drawn through ϵ_c–T_g data for polymer–dichlorobenzene mixtures; this line also served to correlate the polystyrene solvent crazing data fairly well.

As with the polymers studied previously a fair correlation exists between ϵ_c and T_g down to a DSC T_g somewhat above ambient (in this case ~50°). All the liquids of DSC $T_g \simeq 61°$ were observed to cause polycarbonate film to whiten. With acetone (DSC T_g = 54°) the whitening is well understood to be caused by polymer crystallization which occurs only when the T_g of the amorphous polymer is reduced below ambient by swelling. We, therefore, believe that all these agents reduce T_g below ambient temperature. Consequently the recorded DSC T_g's are estimated to be at least 30° higher than the T_g's of the swollen, but still amorphous, polymer specimens measured on a time scale appropriate for the crystallization process.[20]

The similarity in behavior of polysulfone and polycarbonate is evident in Figure 3 again. Were the T_g's of the two pure polymers the same, their resistance to craze initiation resistance would be identical in air and in all swelling environments that reduce T_g to temperatures as low as ambient. Values of $d\epsilon_c/dT_g$ are about one-third as great for poly(phenylene oxide) and polystyrene as for polycarbonate and polysulfone.

We are not certain of the source of this difference in $d\epsilon_c/dT_g$ for the two pairs of polymers. It may be significant, however, that neither polystyrene nor poly(phenylene oxide) exhibit large low-temperature modulus relaxations while the so-called β relaxations for polysulfone and polycarbonate are prominent. Two other amorphous polymers previously subject to crazing studies, poly(vinyl chloride) (PVC and poly(methyl methacrylate) (PMMA), exhibit prominent β relaxations. While data of the kind used in Figure 3 are available for neither polymer, it may be significant that critical strains in air for the two are about 1.8[10] and 1.0%,[14] respectively. The DSC T_g's of PVC and PMMA are approximately 90 and 110°, respectively. If, as with the polymers compared in Figure 3, the critical strains of PVC and PMMA in organic liquids fall to their minimum values at DSC T_g's of 40–50°, values of $d\epsilon_c/dT_g$ would be the same as or greater than those for polycarbonate and polysulfone.

A low-temperature secondary relaxation of modulus is

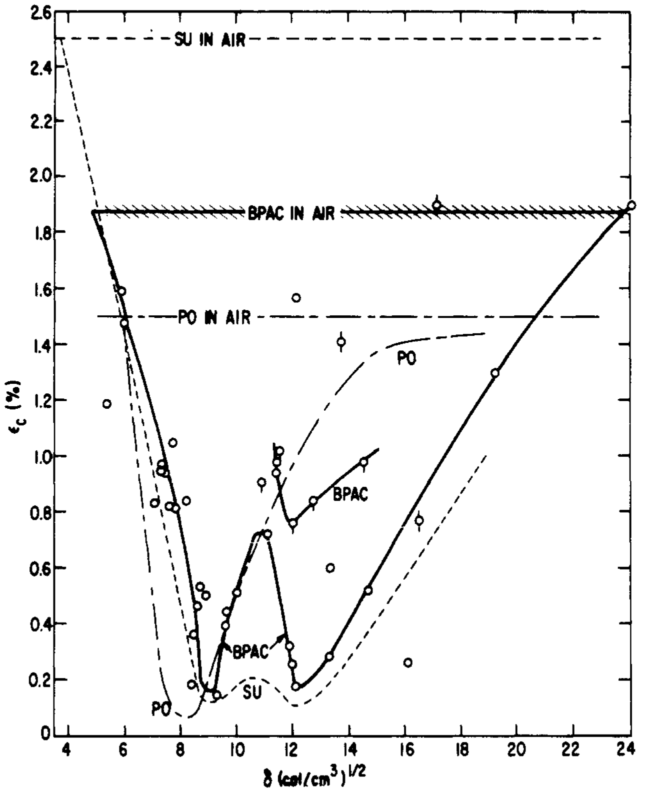

Figure 4. Critical strain ϵ_c for crazing or cracking of polycarbonate *vs.* δ of liquid organic agent. Circles, data of this study; single tab, monohydric alcohol; double tab, dihydric alcohol. Solid line (BPAC), correlation line for these data; broken lines, correlations for poly(phenylene oxide) (PO) and polysulfone (SU) taken from previous studies.[2a,b]

currently understood to be accompanied by a relaxation in yield stress.[21] Since yield stress is simply the stress at which the rate of an elastic deformation in a constant strain rate test equals the machine extension rate,[22] the following conclusion can be inferred. A low-temperature modulus relaxation is a sign indicating an increased ability at higher temperatures to deform anelastically (*i.e.*, to creep) at the intermediate and high stress levels where crazing is otherwise likely to initiate. If these inferences are correct, polymers having greater homogeneous creep rates, as well as higher glass temperatures, are likely to be the most resistant to craze formation in the absence of organic agents. Creep data for testing this inference are limited. It has been pointed out elsewhere,[14] however, that creep rates for polystyrene are lower than those for PMMA under comparable stresses.

Finally, if the ability to creep is important in determining crazing resistance, a complete description of solvent crazing will require an understanding of how organic diluents affect the ease of homogeneous flow of glassy polymers independent of any reductions in glass temperatures.

Correlation between Critical Strain and Solvent Solubility Parameters. The correlation between ϵ_c and δ_s for these polycarbonate crazing data (Figure 4) is much less perfect than that for poly(phenylene oxide). A broad outline of crazing behavior in small molecule liquids is evident nevertheless. The crazing resistance data fall on a curve that exhibits minima at $\delta_s \simeq 9$ and $\delta_s \simeq 12$ (alcohols excepted); these values of δ_s are approximately those at which the junction of the base and the spike of the swelling envelope occurs. Thus crazing resistance is a minimum in those liquids swelling the polymer just enough to lower T_g to ambient temperature. Liquids lying between $\delta_s = 9$ and 12 appear to swell the polymer rapidly and heavily, transforming it to a rubber. Similar, although less pronounced, behavior (dotted line) was seen with polysulfone. Several aspects of this process are likely to prevent crazes from initiating at the lower strains and longer times: (a) elastic strain reduction due to the volume increases; (b) homogeneous stress relaxation; and (c) the increase in Poisson's ratio μ toward 0.5. The larger is μ the lower are the cavitational stresses generated at flaws by a given level of applied uniaxial tension.

The minima in polycarbonate crazing resistance are located equidistant from $\delta_s = 10.5$ which is the approximate position of maximum swelling seen in Figure 1. Thus, as expected, the center of the polycarbonate crazing correlation line is located to the right of that for poly(phenylene oxide) in correspondence with the greater solubility parameter of polycarbonate. However, the resistance of polycarbonate and polysulfone to crazing in media of low δ_s is not as much greater than that of poly(phenylene oxide) as would have been predicted *a priori* on the basis of a comparison of δ_p values alone. The reason for this, of course, lies in the greater breadths of the swelling envelopes of the two compared to that for poly(phenylene oxide).

As with polysulfone, monohydric alcohols are less potent crazing agents for polycarbonate than are aprotic liquids having the same values of δ_s. Of course, this is a simple consequence of the lower solubility of the alcohols in the polymer. And the lower solubilities of the dihydric alcohols make these liquids even poorer crazing agents. Finally, the molecular size effects that were seen to affect swelling by the alcohols carry through to their crazing behavior. Although a minimum in crazing resistance in monohydric alcohols occurs at $\delta_s = 12.0$ also, the minimum in contrast with the two previously discussed is caused by a *maximum* in solubility rather than the rise in importance of other modes of stress relaxation.

With polysulfone, polystyrene, and polycarbonate the usefulness of ϵ_c–δ_s plots is limited for two reasons primarily. First, solubilities are not adequately predicted by a naive use of solubility parameter, an observation made many times by previous authors. Second, as δ_s approaches δ_p, swelling beyond the level necessary to reduce T_g to ambient produces a reversal in the trend of critical strain the degree of which is not currently predictable.

IV. Conclusions

Our major conclusions from this and previous studies of solvent crazing are as follows. (1) When strained and then immersed in swelling agents the crazing resistances of polycarbonate and other glassy polymers are reduced roughly linearly with the reduction in T_g eventually obtained at equilibrium degree of swelling. Sources of scatter in these correlations have not been assessed although both experimental errors in ϵ_c and T_g measurements and intrinsic variations from molecule to molecule in effects on ductility per unit of swelling are probably involved. (2) The degrees of swelling involved in reducing crazing resistance toward its minimum are not great enough to induce polycarbonate crystallization. Thus there is no unique cause-and-effect relationship between crystallization and crazing or cracking in polycarbonate. (3) Swelling characteristics of polycarbonate are very similar to those of polysulfone because of the similarity of T_g's and solubility parameters of these polymers. As with other glassy polymers the swelling profile for non-hydrogen-bonded small-molecule liquids is centered on the solubility parameter of polycarbonate and is substantially broadened at low degrees of swelling due to the excess free energy of the glassy state. Both hydrogen bonding and molecular size cause aberrations in swelling behavior. (4) Because of these aberrations and the inability to predict from polymer structure and T_g alone swelling profile magnitudes (particularly the all-important glassy portions of these) it is not possible currently to predict the solvent crazing resistance of a hitherto untested polymer across the whole spectrum of organic liquids. (5) Resistance to crazing in the absence of organic liquids correlates with two quantities: (a) T_g (the higher the better) and (b) the existence of low-temperature relaxations that reduce yield stress and make homogeneous creep occur more easily.

References and Notes

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(11) With acetone as the swelling agent crystallization reduces the degree of swelling in polycarbonate by 40%; that is, solubility is not proportional to the noncrystalline fraction of polymer.[4] Effects of this kind could be expected to vary from one swelling liquid to the next, depending on the degree to which each allows crystallinity to develop.

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(13) In the molding of the sheets polymer pellets were usually piled up in the center of the mold so that, upon closing the press, a degree of flow would occur that would improve the knitting together of the pellets and the elimination of air bubbles. The flow thus tended to be radial; consequently, orientation is likely to have varied from point to point in the sheet both in direction and magnitude. Orientation in the direction in which the crazing stress is subsequently applied tends to produce increased resistance to crazing while orientation transverse to the applied stress tends to produce a decreased crazing resistance.[14] For a given *degree* of orientation, however, the *decrease* produced by transverse orientation is known to be considerably smaller than the *increase* produced by parallel orientation.

(14) R. P. Kambour, *J. Polym. Sci. Macromol. Rev.*, 7, 1 (1973).

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(16) Evidence from which polymer-polymer miscibility may be inferred is found in ref 17.

(17) B. P. Barth, U. S. Patent 3,365,517, Jan 23, 1968.

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(19) These latter T_g's were measured on swollen-but-still amorphous polymer in torsion pendulum tests at 1 Hz;[4] since the maximum in log decrement for the dry amorphous polymer occurred at 151°—7° lower than the T_g determined by scanning calorimetry—the torsion pendulum T_g's have been adjusted by arbitrarily adding 7° to each. The crosses in Figure 2 are plotted from these adjusted values.

(20) This discrepancy points up one of the difficulties inherent in the procedures leading to the kind of correlation attempted here. The time scales for the various measurements and observations are not the same. With dry polymer the crazing measurement is complete in about 24 hr but with liquids like acetone crazing and cracking do not proceed beyond a minute or so. Calorimetric glass temperatures are all measured at the same scan rate but the completion of crystallization requires times of the order of a minute to a day depending on the degree of swelling.

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Notes

Infinite-Dilution Viscoelastic Properties of Randomly Branched Polystyrenes

NORIO NEMOTO, YUTAKA MITSUDA, JOHN L. SCHRAG, and JOHN D. FERRY*

Department of Chemistry and Rheology Research Center, University of Wisconsin, Madison, Wisconsin 53706.

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Measurements of storage and loss shear moduli of dilute polymer solutions, taken in a frequency range near the reciprocal of the terminal relaxation time and extrapolated to infinite dilution, provide data which are sensitive to long-chain branching and should clearly distinguish even one branch point per molecule provided the molecular weight distribution is fairly narrow.[1-5] Studies of certain ethylene-propylene terpolymers[4] have provided estimates of the degree of branching which were plausible in the light of their compositions, but could not be compared with quantitative information from an independent source. In the absence of theory for randomly branched polymers, the reduced intrinsic steady-state compliance was compared with that calculated for comb polymers of regular structure by the method introduced by Osaki,[6] modified from the theory of Zimm and Kilb.[7] In this calculation, the steady-state compliance is found to be a monotonically decreasing function of the number of branch points per molecule and of the fraction of molecular mass present in the branches. It is assumed that the randomly branched polymer will correspond roughly to a comb in which the branch lengths and the backbone spacings between branches are equal, and the value of f (branch points per molecule) is chosen which matches the experimentally determined steady-state compliances after correction for molecular weight heterogeneity.

In the present report, data are given for three randomly branched polystyrenes whose average degrees of branching were known from a kinetic analysis of the polymerization mechanism.[8] These samples were generously given us by Professor S. Onogi and Dr. T. Masuda of Kyoto University, together with data for their characterization, which are presented in Table I. The number of branch points per molecule from the polymerization kinetics, denoted by $\bar{M}_n/M_b$, ranged from 1.9 to 17. The number-average molecular weight $\bar{M}_n$ was determined by osmometry, and the ratio $\bar{M}_w/\bar{M}_n$ by gel chromatography.

Aroclor 1232 was used as a solvent for all three samples, and *o*-xylene was also used for RB-24, which had the highest molecular weight, to extend the measurements into the terminal zone. Their viscosities, η_s, at 25.0° were 0.1005 and 0.00753 P, respectively; their densities 1.2686 and 0.8760, respectively. Intrinsic viscosities, $[\eta]$, were obtained from the viscoelastic measurements at low frequencies, and in one case $[\eta]$ was also measured by capillary viscometry and found to be in reasonable agreement. These values are also given in Table I. For sample RB-24 the difference between the intrinsic viscosities in the two solvents indicates that *o*-xylene is a slightly better solvent. All viscoelastic measurements were made at 25.00°