Coalescence of the ionomer domains occurs during the time spent in the viscous melt. However, the coarsening of the dispersed ionomer appears to be accelerated when the sample is repeatedly melted and crystallized. This suggests that a crystallization-induced type of coalescence is also occurring. A combination of these two effects results in a linear increase of the domain size with time as a sample is repeatedly melted for 10 min and crystallized. This coalescence phenomenon as well as the "speed" of the crystallizing front is shown to have an effect on the radial growth rate of the polypropylene spherulites. A radial growth rate depression occurs as the spherulite is rejecting the second component, the effectiveness of which is dependent on the crystallization temperature. Maximum growth rates are observed at the point where the rejection of the dispersed domains is at a minimum or the size of the dispersed phase is well above that critical size required for rejection. Once the domain size is greater than the critical size, coalescence occurs predominantly in the melt. After this point, the radial growth rate decreases as the ionomer domain size is increased. This radial growth rate decrease beyond that maximum cannot be explained using the equations for rejection, engulfment, and deformation.

Future work will involve studies of the influence of the chemical characteristics of the ionomer (such as functionalities, neutralization, etc.) on the crystallization and coalescence phenomena of polypropylene/polyethylene-based ionomer blends. By modifying the chemical structure of the ionomer, the interfacial free energy between the matrix polymer and the dispersed phase will be changed, which would yield more information about the importance of interfacial energies on the crystallization kinetics of an immiscible blend.

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Notes

Variable-Temperature FT-IR Studies of Organic Carbonate Solutions

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Introduction

Although the intermolecular structure of amorphous Bisphenol A polycarbonate (BPAPC) is ill-defined, a number of smaller, well-characterized BPA-based carbonate systems have been examined extensively.[1] These past efforts have been oriented toward understanding how variations in fundamental conformation and structural packing at the molecular level are manifested in the macroscopic properties of these materials. Such intra- and intermolecular interactions in BPAPC analogues have been studied by a variety of techniques (principally, NMR, X-ray spectroscopy, and quantum mechanical calculations). To date, no experimental work has been reported on BPAPC using low-temperature solution IR methods.

This paper summarizes our observations of both monomeric and polycarbonate solutions using variable-temperature infrared spectral analysis (VT-IR). These

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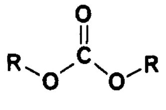
studies are an extension of work directed toward understanding carbonate systems that exhibit the conformational interconversion of the *E,E* (**1**; C_{2v}) and *E,Z* (**2**; C_s)



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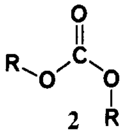

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isomers.[2] At low temperature in methylene chloride (~-90 °C), a number of anomalous absorptions are observed. These novel bands are discussed in terms of a crystalline, structural ordering, which occurs at low temperature.

Experimental Section

All the monomeric organic carbonates were purchased from Aldrich and purified by standard procedures[3] prior to their use. The polycarbonate was commercial GE LEXAN; the material used had a 0.53 IV, M_w = 27 400,[4] and a dispersity (M_w/M_n) of 2.56. The methylene chloride and acetonitrile were anhydrous EM SCIENCE OmniSolv grade solvents, which had been stored over 3-Å molecular sieves.

The infrared work was performed on a Nicolet 7199 FT-IR spectrometer with an MCT (HgCdTe) detector. The data were taken at a 1-wavelength resolution. A total of 256 scans were acquired prior to transformation, and the resulting spectra were plotted without smoothing or base-line correction. The IR cell was a SPECAC P/N 21.000 variable-temperature solution cell, with a 0.1-mm cell path length and AgCl windows. The spectrometer, including the chamber containing the VT-IR cell, was purged constantly with anhydrous nitrogen during both the cool-down and the acquisition periods. This precaution both precludes the condensation of atmospheric moisture on the cell windows and eliminates measurement of background atmospheric CO_2 and H_2O. The FT-IR spectra were obtained at +20, -20, -30, -50, -80, and -90 °C. All measurements were made with an accuracy of ±3 °C. All nonvariable-temperature infrared measurements were made with a Perkin-Elmer Model 598 IR spectrometer.

Results and Discussion

Evidence of conformational isomerization in organic carbonate esters, resulting from rotation about the carbon–oxygen bond, has been sought by a number of investigators. The conformational equilibrium populations and corresponding rotational energies have been studied for both monomeric[5] and polymeric[1] carbonates. The measured rotational free energy barriers for the interconversion of the *E,E* (**1**; C_{2v}) and *E,Z* (**2**; C_s) conformers range from 5.4 to 8.6 kcal mol^{-1}. Generally, the enthalpy difference between these two conformations is on the order of 1.3 to >2.6 kcal mol^{-1}. Our studies have focused on developing solution IR methodology as a sensitive probe for differentiating between such conformational isomers.

Infrared monitoring techniques were utilized for two reasons: (i) interconverting species do not rotationally average on the time scale of the infrared measurement and (ii) the energy absorptions in the infrared region reflect specific vibrational modes, which are characteristic of certain functional groups. Variable-temperature (low-temperature) procedures were employed to improve peak resolution by minimizing the thermally induced vibronic broadening.

As part of our studies into the conformational equilibrium of the polycarbonate carbonyl group, we examined its solution behavior in both methylene chloride and acetonitrile. No change in the infrared spectra was observed in any of the acetonitrile solutions as a function of temperature; all VT spectra were indistinguishable from their corresponding room-temperature solution spectrum. However, as the methylene chloride solutions were cooled below -80 °C, anomalous absorption bands were observed; similar variable-temperature experiments using only the methylene chloride solvent exhibited none of these new bands. Furthermore, the measured samples were loaded and run under an anhydrous nitrogen atmosphere to preclude the condensation of atmospheric moisture and/or carbon dioxide (2340 cm^{-1}).

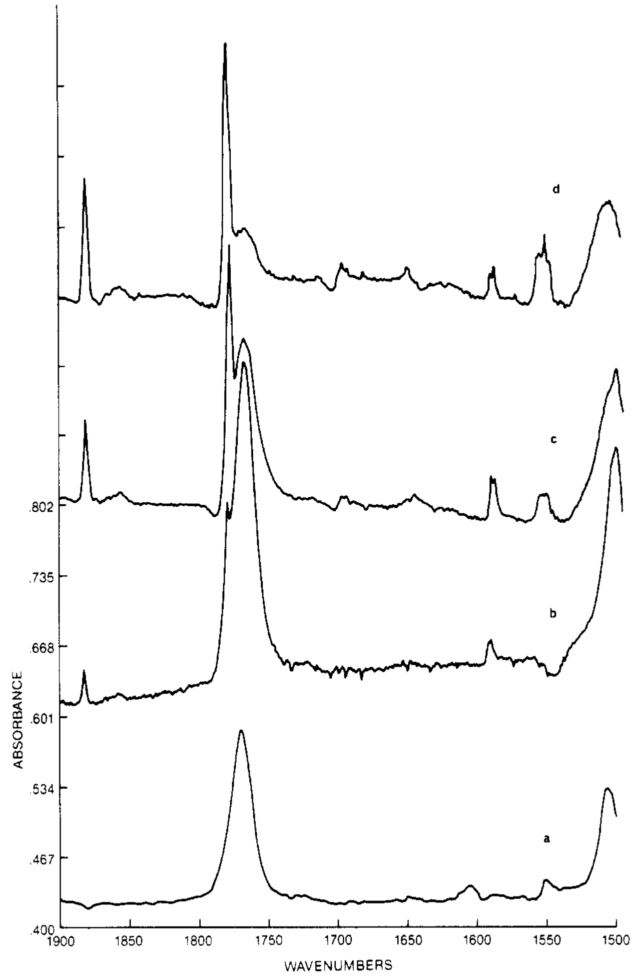

Figure 1. Temperature-dependent infrared spectra of BPAPC in methylene chloride (a) at room temperature (initial solution), (b) at -90 °C for 5 min, (c) at -90 °C for 30 min, and (d) at -90 °C for 1 h.

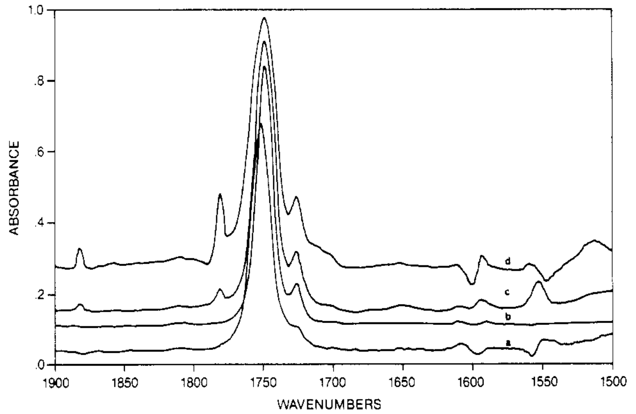

Figure 2. Temperature-dependent infrared spectra of dimethyl carbonate in methylene chloride (a) at room temperature, (b) at -80 °C for 15 min, (c) at -90 °C for 15 min, and (d) at -90 °C for 45 min.

Table I
Characteristic Infrared Absorption Bands of Organic Carbonates in Methylene Chloride at -90 °C for the Spectral Region 1900–1550 cm^{-1}

carbonate[a]	infrared absorption frequencies, cm^{-1}							
DMC[b]	1882 (m)	1781 (s)	1749 (vs)	1726 (s)	1650 (m)	1610 (w)	1594 (m)	1554 (m)
			1752 (vs)	1726 (w)				
DEC	1882 (s)	1781 (vs)	1738 (vs)	1700 (w)	1650 (m)		1594 (m)	1556 (m)
			1738 (vs)					
DPC	1882 (s)	1780 (vs)	1758 (s)		1650 (w)	1598 (m)	1593 (s)	1554 (m)
		1780 (vs)	1760 (m)			1601 (m)	1594 (m)	
DPC[c]		1773 (vs)	1750 (s)			1596 (m)	1589 (s)	
BPAPC	1882 (s)	1779 (vs)	1769 (s)	1700 (w)	1649 (w)		1593 (s)	1558 (m)
			1772 (vs)			1604 (m)		

[a] DMC = dimethyl carbonate, DEC = diethyl carbonate, DPC = diphenyl carbonate, and BPAPC = Bisphenol A derived polycarbonate. [b] The first row for each compound lists the absorptions at -90 °C; the second row lists the room-temperature absorptions for comparative purposes. [c] Crystalline DPC (KBr and single crystal) for comparative purposes.

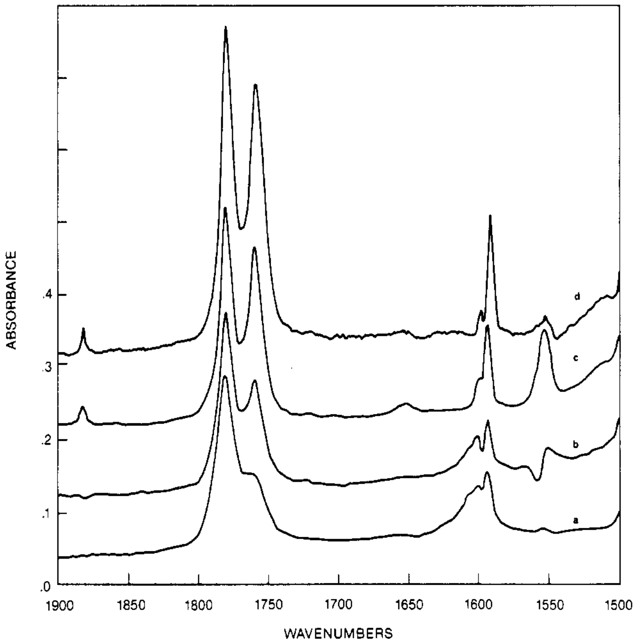

Figure 3. Temperature-dependent infrared spectra of diphenyl carbonate (dilute; 1 × 10^{-3} M) in methylene chloride (a) at room temperature, (b) at -60 °C, (c) at -90 °C for 15 min, and (d) at -90 °C for 45 min.

The spectra of the novel absorptions for the BPAPC solution are shown in Figure 1. In the carbonyl region, the new bands are found at 1882, 1779, 1700, 1593, and 1558 cm^{-1}. These new bands formed gradually as the sample was held at -80 °C or below and continued to increase in intensity over time; allowing this cooled VT-IR cell to warm to ambient temperature caused the observed spectrum to revert to that of the initial room-temperature spectrum. By analogy to the monomeric carbonate systems,[5] it is assumed that this gradual appearance of new absorptions corresponds to the slow crystallization of polycarbonate from solution onto the AgCl windows.[6] The same phenomenon is not observed in the room-temperature IR spectra of BPAPC films containing ca. 24% crystalline polycarbonate; these opaque crystalline BPAPC films were prepared by slow evaporation from solution at room temperature.[1e] Quiescent crystallization of polymers from solution often results in crystallite growth with only local order (e.g., spherulites). Crystallization of BPAPC within the amorphous BPAPC matrix at room temperature probably forms molecular structures that lack the long-range order or orientation necessary to produce the structure observed in our low-temperature spectra. Thus, it appears that simple crystallization of BPAPC is insufficient to explain these new bands.

To facilitate spectral analysis, symmetric monomeric carbonates were examined under our VT conditions as well; in this fashion one could minimize the number of inter- and intramolecular interactions (which might complicate the spectra). The variable-temperature FT-IR solution spectra of dimethyl carbonate (DMC) have been studied in great detail by Katon et al.,[5a,b,e] as part of their investigations into conformational equilibria in the fluid state. Their polarized infrared and Raman data established that the crystallization of DMC produces an oriented polycrystalline film at low temperature. The repetition of the earlier DMC experiments under our conditions allowed the direct comparison of our data with Katon's work. The DMC absorptions characteristic of these low-temperature oriented films are observed at 1882, 1781, 1594, and 1554 cm^{-1} (Figure 2). Due to the freezing point limitation of our solvent (CH_2Cl_2; mp -97 °C), a high conversion of the soluble dimethyl carbonate to the polycrystalline form could not be attained; the original study involved a neat solution, which only exhibited an appreciable amount of the polycrystalline material at ~140 K.[5e] However, this tendency toward orientation in monomeric organic carbonates is found to be quite general. A tabulation of the diagnostic bands in the carbonyl region for a series of alkyl and aryl carbonates is shown in Table I. Oriented polycrystalline materials have also been observed for chloroformate compounds under similar conditions.[7]

The corresponding low-temperature spectra for diphenyl carbonate (DPC) showed absorptions analogous to those observed in the BPAPC. These peaks occurred at 1882, 1650, 1593, and 1554 cm^{-1}; the expected band at ~1780 cm^{-1} is usually obscured by the residual, soluble DPC carbonyl absorption. When the concentration of DPC in solution was less than 2 × 10^{-3} M, the presence of both the *E,E* (1780 cm^{-1}) and *E,Z* (1758 cm^{-1}) conformational isomers is observed (only a trace amount of crystalline deposit is present; Figure 3). Thus, it appears that adroit manipulation of the initial carbonate concentration allows the observation of either conformational isomers or the gradual crystallization phenomenon.

To verify that a higher intermolecular ordering might be a requisite for the observation of these anomalous bands, crystalline DPC was examined.[8] None of the new IR absorptions were observed when crystalline DPC was examined in the solid state (KBr pellet and oriented single crystal). Inspection of the DPC molecules within the crystal lattice indicates their intermolecular arrangement may lack the proper orientation necessary to produce the infrared modes observed here.[11] The observed infrared modes

Macromolecules **1990,** *23,* 348–350

may be a manifestation of either an extended molecular array or short-range configurational interactions. A highly structured, extended array of molecules such as that found in a β-structure (pleated sheet), a liquid crystal, or Langmuir–Blodgett type molecular orientation[9] at the AgCl surface may account for the anomalous peaks. Alternatively, the simple repetition of a head–tail arrangement of the carbonyl units should lead to highly ordered materials. In the absence of a known crystal structure, the exact assignment of the observed bands would be impossible. However, by analogy to dimethyl carbonate crystallized at low temperature, the site symmetry around the carbonate moiety would be anticipated to have lower than C_{2v} symmetry.[5e,g]

Summary

The use of solution VT-IR methodology indicates the occurrence of polycrystalline films from both polymeric and monomeric organic carbonates at low temperature. BPA polycarbonate solutions are found to behave analogously to those of the simple, monomeric carbonates. As suggested by earlier researchers,[5] simple crystallinity within these materials is insufficient to explain the observed results. The low-temperature solution preparation of these oriented polycrystalline films is demonstrated to be both general and quite facile.

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Registry No. LEXAN, 24936-68-3; DMC, 616-38-6; DEC, 105-58-8; DPC, 102-09-0.

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(6) Neither solvent produces any new bands in this region upon cooling. Condensation of atmospheric moisture on the cell windows was not observed during our experiments. Due to the necessity of subtracting the methylene chloride (solvent) spectrum from the data, only the infrared region from ~2000 to 1550 cm^{-1} could be analyzed reliably.

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(8) The diphenyl carbonate used for solid analysis was recrystallized from anhydrous ethanol.[3] The DPC crystallizes to form an orthorhombic lattice with four molecules in the unit cell. The space group is $P2_12_12_1$ with the following lattice constants: a, 6.077 (2) Å, b, 7.297 (1) Å, c, 23.4297 (7) Å; $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$. The calculated density was 1.37 g cm^{-3}, and the data were reduced to an R value = 0.0543 with an R_w = 0.0687. The solid-state conformation of DPC and its extended intermolecular relationships have been published previously.[1i]

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Surface Investigation by ESCA of Poly(ethylene terephthalate)–Perfluoro Polyether Block Copolymers

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Introduction

In the last few years there has been increasing interest in the synthesis of polymeric structures containing fluorine atoms in the chain in order to increase the thermoxidative and chemical resistance and to have low surface energy and a low coefficient of friction. Fluorine atoms can be introduced into polymers by different ways, which in turn can influence the properties of the resulting materials. The recent availability of telechelic perfluoro polyethers (PFPEs) having the general formula $XCF_2(OC_2F_4)_m(OCF_2)_nOCF_2X$ with $m/n = 0.7$ and X = CF_3 (Fomblin Z) and $COOCH_3$ (Fomblin ZDEAL) allows the preparation of polymeric materials containing PFPE, with the possibility of obtaining PFPE blocks bonded to other polymer chains. The presence of a fraction of PFPE as a block copolymer may improve the properties of the resulting heterophase material and could also influence the concentration of PFPE on the surface. Recently, samples consisting of poly(ethylene terephthalate) (PET) and PFPE homopolymers and containing a fraction of PET–PFPE block copolymers have been prepared by the addition of Fomblin ZDEAL (a PFPE with X = $COOCH_3$) during the polymerization of PET via transesterification reactions. Fluorine elemental analysis and selective extractions were employed to characterize the composition of these samples.[1,2] The results showed that at least a part of ZDEAL reacts with the PET chains lead-

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