Solvent-Vapor-Induced Crystallization of Branched Polydisperse Polycarbonate

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Synopsis

Preliminary results on the investigation of solvent-vapor-induced crystallization of polycarbonate /PC/ are presented. The influence of solvent solubility parameters δ_s on the sphrulite radius R and crystallinity degree α is taken into account. It has been found that both R and α depend on δ_s for PC samples of different molecular characteristics.

INTRODUCTION

Many polymer properties are affected by environmental media, and solvent-induced crystallization is often responsible for such effects. Bisphenol A polycarbonate (PC) is one of the important engineering polymers which is sensitive to many common solvents. Various problems of solvent induced crystallization in PC were investigated using both immersion and solvent vapor techniques,[1-10] mainly from the point of view of kinetics of crystallization.

In our recent studies on PC, the morphology was taken into account.[11-13] In this paper morphological aspects of the dependence of solvent-vapor-induced crystallization on the solubility parameter of solvents is briefly discussed.

EXPERIMENTAL

Material

Four PC samples differing in molecular characteristics were investigated; two of them, RT-491 (linear) and DE-8 (branched) were prepared by interfacial polycondensation; the other were commercial samples of Makrolon 2405 (Bayer A.G.) and Lexan 151 (General Electric Co.) supposed to be linear and branched, respectively. The samples were characterized by the weight average molecular weight $\overline{M}_w$, polydispersity degree $q = \overline{M}_w/\overline{M}_n$, branching degree G (the ratio of intrinsic viscosities of branched and linear molecules of the same molecular weight), and microgel factor G' as a measure of microgel content. The conventional wide angle light scattering (LS),[14] gel permeation chromatography (GPC), and viscometric measurements[15] were used, respectively.

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Crystallization

Each PC sample was moulded in a laboratory compression molding equipment within 5 min at temperature about 20°C higher than the melting temperature of the sample (determined on the hot stage of polarizing microscope). Then the sample was rapidly cooled down to room temperature and, in the form of thin amorphous film, was kept 24 h in a desiccator in a solvent vapor – air atmosphere to induce crystallization. Nitromethane, acetone, and ethyl acetate were chosen as crystallizing solvents.

Measurements

Small angle light scattering (SALS) and density measurements were performed on solvent vapour crystallized PC samples.

A laboratory SALS instrument with an He–Ne laser was used for measurements of spherulitic structure patterns. The angle of maximum scattered light intensity θ_m was determined from the photometer scan taken at 45° azimuthal direction. The spherulite radius R (μm) was calculated from the following formula[16]:

$$R = 4.1\,\lambda\,/4\pi\,\sin(\theta m/2) \tag{1}$$

where $\lambda = 0.6328$ μm is the light wavelength.

The density ρ was measured in a density gradient column with KJ solutions. Then the crystallinity degree α (%) was calculated from the following equation:

$$\alpha = [(\rho - \rho_a)/(\rho_c - \rho_a)] \times 100 \tag{2}$$

where ρ is the measured density of crystallized sample, ρ_a is the measured density of amorphized sample, and $\rho_c = 1.31$ g/cm^3 is the density of crystalline PC.[17]

RESULTS AND DISCUSSION

The molecular characteristics of PC samples are shown in Table I. We have tried to correlate the observed solvent-vapor-induced crystallization effects with the differences in solvent affinities to PC, using the solubility parameter δ in a way similar to that applied for critical strains in poly(phenylane oxide) (PPO).[18] The solubility parameters of the polymer, δ_p, and solvents, δ_s, are shown in Table II.[17,19] The plot of R vs. δ_s (Fig. 1) indicates that the same R is obtained for all samples in the solvent vapor atmosphere, independently of molecular characteristics of PC samples, if the solubility parameters of the polymer and a solvent are of the same order, $\delta_s \simeq \delta_p$. The plot of α vs. δ_s (Fig. 2) suggests an existence of maximum crystallinity degree for $\delta_s \simeq \delta_p$. Thus the maximum crystallinity degree for PC at $\delta_s = \delta_p$ coincide with the minimum critical strain for PPO at $\delta_s = \delta_p$.[18] It is reasonable that macromolecules unstrained by any thermo dynamic difference to the surroundings can align themselves to the highest possible crystallinity degree.

TABLE I
Molecular Characteristics of PC Samples

Sample	Molecular weights $\bar{M}_w \times 10^{-3}$ GPC	Molecular weights $\bar{M}_{wL} \times 10^{-3}$ LS	Polydispersity degree q	Branching degree G	Microgel factor $G' \times 10^{-3}$
Linear					
A Makrolon 2405	25.9	22.2	2.5	1.01	0
B RT-491	39.2	26.3	2.5	0.99	1.0
Branched					
C Lexan 151	42.8	38.9	4.7	0.92	1.2
D DE-8	59.3	38.7	3.9	0.83	3.0

TABLE II
Solubility Parameters

Substance	Solubility parameter δ [(cal/cm^3)$^{1/2}$]	Solubility parameter $\delta \times 10^{-3}$ [(J/m^3)$^{1/2}$]	Ref.
Polycarbonate			
Single value	9.9	20.3	17
In p solvents[a]	9.5–10.6	19.5–21.7	19
In m solvents	9.3– 9.9	19.1–20.3	19
Nitromethane, p	12.7	26.0	19
Acetone, m	9.9	20.3	19
Ethyl acetate, m	9.1	18.7	19

[a] p = poorly hydrogen bonded; m = moderately hydrogen bonded.

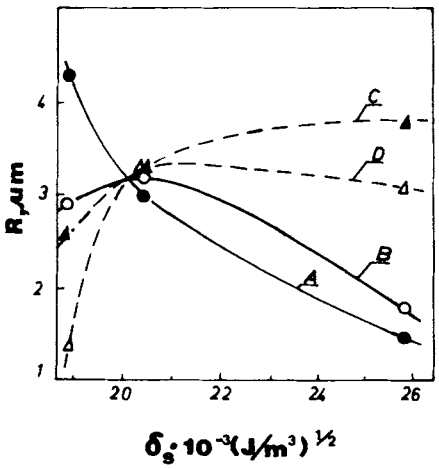

Fig. 1. Spherulite radius R vs solubility parameter δ_s: (—) linear PC samples; (– – –) branched PC samples; (A) Makrolon 2405 (●); (B) RT-491 (○; (C) Lexan 151 (▲); (D) DE-8 (△).

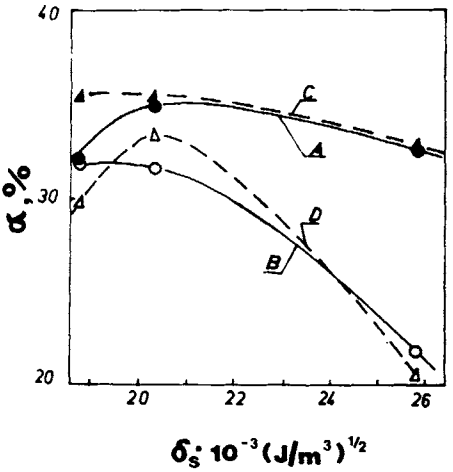

Fig. 2. Crystallinity degree α vs. solubility parameter δ_s. Symbols are as in Figure 1.

As can be expected, the nature of a solvent and its affinity to the polymer are the most important parameters for solvent-vapor-induced crystallization of PC. However, the influence of molecular characteristics such as molecular weight, molecular weight distribution, long chain branching, and microgel content is difficult to distinguish, since the number of samples was limited in our preliminary investigation. Anyway the problem of solvent-vapor-induced crystallization seems to be very important from the point of view of the influence of atmosphere pollution on PC articles. Therefore, the investigation will be continued.

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