Surfactant-Induced Crystallization of Polycarbonate

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Introduction

Crystallization in polymers can generally be induced and controlled by several means such as by adding nucleating agents or plasticizers, thermal annealing, pressure, and solvent vapor exposure. Whereas the first two methods are commonly used in industrial processes as well as for studying the fundamentals of the crystallization behavior, the number of polymers studied by solvent vapor-induced crystallization is limited. Some of the examples of the latter are poly(ethylene terephthalate) (PET),[1] polystyrene (PS),[2,3] and polycarbonate[4−6] (PC). It is well-known that crystallization of pure polycarbonate is extremely slow,[7] with a crystallization half-time of 12 days at 190 °C. Although this time is significantly reduced with the aid of plasticizers, high-temperature annealing in the range 150−190 °C is still required. Recently, Tsuburaya and Saito[8] reported crystallization of polycarbonate induced by blending with poly(ethylene oxide). With a high molecular weight PEO, and crystallization temperatures of 140 and 180 °C, maximum crystallization was achieved in 400 and 200 s, respectively. Thus, high temperatures are required to crystallize polycarbonate, even in the presence of plasticizers.

There have been several studies reported recently on the surfactant-induced mesomorphic structures in polymer−surfactant systems.[9−14] Ruokolainen et al.[9,10] discussed the mesomorphic structures resulting from the complexation of atactic poly(4-vinylpyridine) (P4VP) with different classes of hydrogen-bonding surfactants. The hydrogen bonding between the side group of the polymer and the surfactant leads to layered structures. In these cases, the polymer itself is not readily crystallizable due to the atactic configuration. It is the organization/crystallization of the surfactant molecules, with hydrogen bonding to the polymer chain, which gives rise to the supramolecular assembly.

In this paper, we describe the crystallization of polycarbonate in the presence of a surfactant, which requires a temperature far less than that reported to date. During the course of our studies[15] on polycarbonate/carbon nanotube composites, we used the surfactant Triton X-100 (polyoxyethylene isooctylcyclohexyl ether) to disperse the nanotubes. We discovered that when films are prepared from methylene chloride solutions of polycarbonate and this surfactant, beyond a certain concentration of Triton X-100 (a liquid with a density of 1.029 g cm^{-3} at room temperature), crystallization of polycarbonate occurred, in as-prepared films. As mentioned above, polycarbonate exhibits a very slow crystallization rate, and annealing for several days at 190 °C or higher is required to impart even a modest crystallinity.[7,16] Crystallization by solvent vapor exposure is somewhat rapid, and solvents such as acetone and methylene chloride and butyl acetate have been used.[4−6] The crystallization of polycarbonate in the presence of a surfactant we believe is interesting and, to our knowledge, has not been reported so far.

Experimental Section

Triton X-100 (reduced) and bisphenol A polycarbonate (M_w = 64 kg/mol, density = 1.20 g/cm^3) were purchased from Aldrich Chemical Co. and used as received. The formula for Triton X-100 (reduced) is 4-(C_8H_{17})-C_6H_{10}-(OCH_2CH_2)$_n$-OH. The 4-(C_8H_{17}) is an isooctyl group attached to the 1 position of the cylcohexyl group (C_6H_{10}), and the (OCH_2CH_2)$_n$ is attached to the 4 position of the cyclohexyl group. There are n oxyethylene groups where n is ~10.

Polycarbonate was dissolved in CH_2Cl_2 (Caledon, Laboratory grade) at room temperature to form a solution of ~15% w/v. Triton X-100 (reduced) was then added using a pipet, and the mixture was sonicated for 10 min (Branson 1510, 70 W). A series of solutions between 0.01 and 13% w/w of Triton X-100/polycarbonate were prepared (corresponding to 0.02−2.5% w/v of surfactant/CH_2Cl_2). The films were cast on a silanized glass plate using an aluminum spreader. They were dried at room temperature for 24 h, followed by drying for 24 h in a vacuum oven at 80 °C. Another set of films (set 2) was dried only at room temperature for several weeks. The resulting films were between 15 and 25 μm thick, and those containing <10% w/w surfactant were clear and flexible. As the percentage increased, the films became brittle and cloudy. Films made from concentrations >11% w/w surfactant did not peel from the glass plate and were collected as a white powder.

Calorimetry was performed using a DuPont 990 DSC calibrated for temperature and area using indium. All thermograms were obtained using a heating rate of 10 °C/min under a nitrogen flow and 7−10 mg of sample. Optical micrographs were obtained using a Zeiss Axioplan-2 imaging microscope under crossed polar conditions. X-ray diffraction data were collected using a Philips automated powder diffractometer, model PW 1710. Nickel-filtered Cu Kα radiation (λ = 1.542 Å) was used. The patterns were recorded with the film mounted on the standard diffractometer sample holder. Although the films were prepared on a glass substrate, they were removed from it for X-ray analysis. The MDI scan 3.2 software (Materials Data Inc., Livermore, CA) was used for data collection. The calculations of the d spacings, intensities, and crystallinity were performed using MDI Jade 5.0 XRD pattern processing software. The crystallinity was calculated by subtracting the background from the total intensity. The diffractometer traces were also recorded with the film turned 90° in its plane with respect to the beam, to confirm that there was no preferred orientation. The diffraction patterns were also recorded on film in transmission mode, using a Statton type Warhus flat film camera under vacuum to eliminate air scatter (William Warhus Co., Wilmington, DE).

Samples for infrared spectroscopy (Bomem Michelson 120 FTIR, resolution 4 cm^{-1}, 600−4000 cm^{-1}) were prepared by evaporating a drop of solution on a NaCl plate, mixing a few milligrams of powder to form a KBr pellet, or using the film without substrate.

Results and Discussion

Figure 1 shows the X-ray diffraction patterns from films/powder (dried at 80 °C for 24 h) corresponding to the concentrations of 5, 10, and 13% Triton. It is seen that while only a broad peak is seen at $2\theta = 17.2°$ with 5 and 10% Triton, the reflection at this angle (d = 5.14

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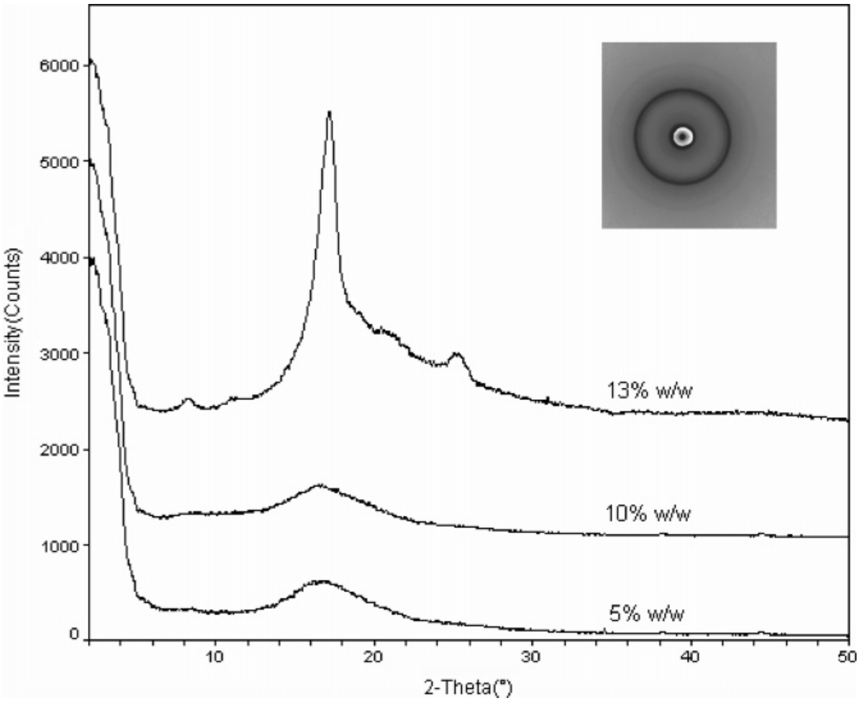

Figure 1. X-ray diffraction patterns from samples with (a) 5, (b) 10, and (c) 13 wt % Triton X-100 in polycarbonate. The inset shows the diffraction recorded on film for the sample with 13 wt %.

Å) becomes a sharp peak with a concentration of 13%. It was found that significant crystallization takes place beginning with a concentration of 11% (w/w). In the diffraction pattern recorded on film (shown as an inset in Figure 1), several crystalline reflections are seen (the numbers in parentheses are the Miller indices) with d = 3.53 [(124), (302), (312)], 4.30 (122), 5.17 (210), 5.60, 7.85 (110), and 10.82 (002) Å. All these reflections, except that with $d = 5.6$ Å, correspond to the orthorhombic crystal form[17] and to those observed by Radhakrishnan et al.[18] with the polycarbonate synthesized by solid-state polycondensation. The reflection at $d = 5.6$ Å might be considered to be similar to the reflections at 5.48 (210) or 5.79 (201) Å of the monoclinic form.[19] However, other reflections for the monoclinic form, e.g., d = 8.05, 4.75, 4.06, and 3.28 Å, are not recorded in this case. (When we exposed the films to methylene chloride vapor, the reflection with $d = 5.6$ Å is present.) Apart from noting that the structure formed here could be a mixture of orthorhombic and monoclinic forms, investigation of the crystal structure itself is beyond the scope of this paper. A crystallinity of 18% was calculated from the diffractometer trace for the polycarbonate film with 13% Triton. The upward turn of the curves at smaller angles is due to air scatter. We could not detect any small-angle reflection with the Warhus camera that we used here.

The results of thermal analysis of the films are shown in Figure 2. It is seen that the T_g of the polycarbonate is depressed significantly with an increase in the concentration of Triton X-100. With 10 wt % Triton, the T_g is reduced to ~80 °C. This is similar to the depression in T_g measured for the polycarbonate, e.g., with the plasticizer tritolyl phosphate (TTP).[20] No melting endotherm is observed until the Triton concentration reaches 11%. As seen from this figure, the heat of fusion increases sharply between 11 and 13% Triton. The ΔH of 21 J/g with 13% Triton is the same as the maximum heat of fusion recorded for samples annealed for several hours at temperatures in the vicinity of 200 °C. However, the present samples were not exposed to such high temperatures. Using a value of 109.7 J/g for the ΔH of 100% crystalline polycarbonate,[21] this leads to a crystallinity of 19.1%. This is in agreement with the crystallinity calculated from X-ray diffraction.

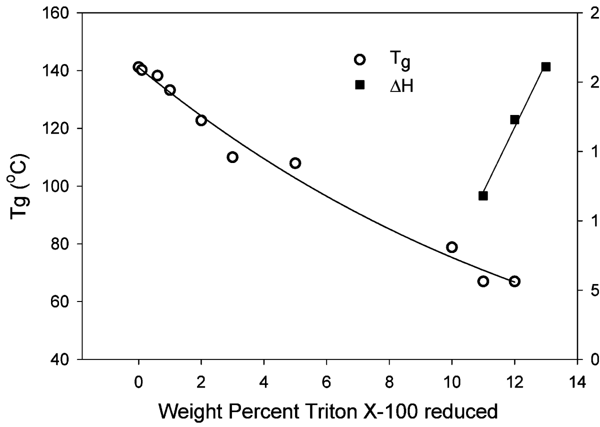

Figure 2. Variation of the T_g of the polycarbonate and the heat of fusion are shown as a function of the concentration of Triron X-100 in polycarbonate.

Parts a and b of Figure 3 show the optical micrographs of the polycarbonate films with 11 and 13% Triton, respectively. The latter shows extensive cracks. The light scattering pattern recorded in the H_v mode for the film with 11% Triton is shown in Figure 3a. This H_v pattern indicates a spherulitic radius of 28 μm, in agreement with the radius of about 25 μm obtained from the optical micrograph. It is seen that the spherulites are concentrated in one region of the film in Figure 3a.

The question arises as to the specific role that the surfactant plays in the crystallization observed in this study. As mentioned above, the mesomorphic order induced by the surfactant in various atactic polymers was due to the hydrogen bonding of the polar group of the surfactant with the side group of the polymer and

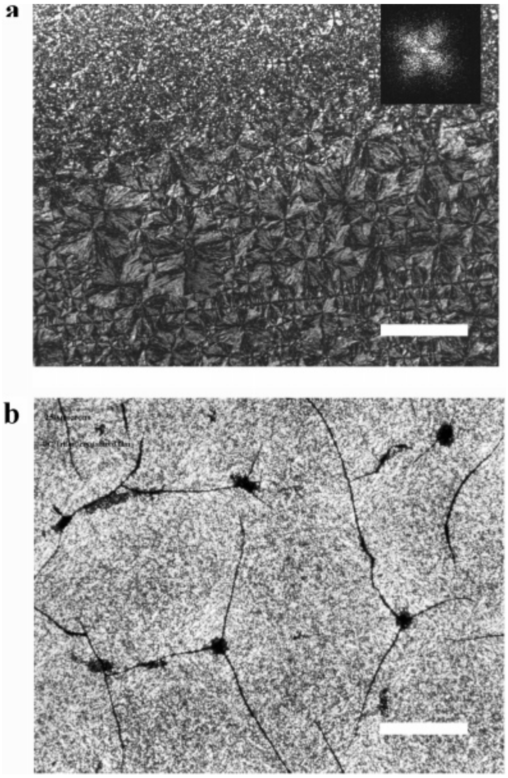

Figure 3. Optical micrographs of samples with (a) 11 and (b) 13 wt % Triton X-100. The H_v mode light scattering pattern is also shown in (a). The scale bar is 250 μm.

the interdigitation of the alkyl segments.[9−13] In the present case, however, the IR spectra did not reveal any specific interactions between the polycarbonate and Triton X-100. The spectrum of the polycarbonate/surfactant system was simply a compound spectrum of the individual components. No shift in the absorption frequencies, e.g., in the carbonyl group, was observed. The X-ray diffraction pattern is representative of the polycarbonate structure[17−19,22] crystallized by annealing, and there is no change in the crystalline conformation of the chain. Optical microscopy did not show any lyotropic behavior of the polycarbonate/Triton X-100 solution.

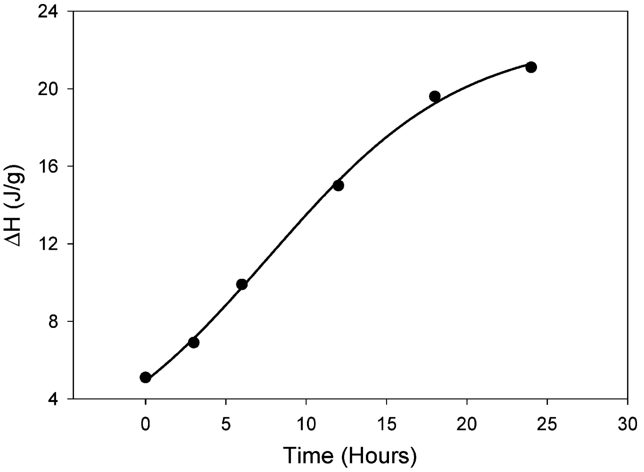

Figure 4. Change of heat of fusion with time of annealing at 80 °C. The initial film (with 13% Triton) was dried at room temperature for several weeks (set 2).

These results, combined with the depression of the T_g of the polycarbonate, lead to the conclusion that Triton X-100, which is a surfactant, acts as a plasticizer. This itself is not new, and several plasticizers are known to crystallize polycarbonate. However, the thermal requirements for crystallization differs from other known results on plasticizer-induced crystallization of polycarbonate. With other plasticizers such as tritolyl phosphate, annealing in the range 150−190 °C is required for crystallization to occur, although the time required is significantly reduced compared to polycarbonate by itself. In the present case, the maximum crystallinity is achieved similar to such high-temperature treatments, although such high temperatures are not used. This suggests that another mechanism could contribute to the crystallization (see below), in addition to the plasticizer effect. Legras et al.[7] showed that in the case of polycarbonate/salt systems the crystallization half-time was reduced to 15 min with 0.25% sodium chlorophenate, when annealed at temperatures noted above. They also showed that the salts chemically interact with the carbonate group, cause chain scission, and form ionic end groups, and these nucleate the crystallization. Thus, the crystallization of polycarbonate in these cases is through chemical reaction rather than through a physical effect. With Triton X-100, the drastic reduction in T_g to below 80 °C facilitates crystallization, when the film is dried at this temperature. It should be noted that even in the case of solid-state polymerization of polycarbonate[18] the reaction is carried out at temperatures in the range 200−230 °C. A reaction time of about 12 h is required for appreciable crystallinity to develop.

The question arises as to whether the use of the chlorinated solvent methylene chloride plays a role in the crystallization. Siegmann and Geil[23] observed that this solvent prevents solvent-induced crystallization during solvent evaporation. Using thin films, they found nodular structure of 60−110 Å in size. Upon annealing at 80 °C, the nodular size increased to several hundred angstroms.

The results discussed above were obtained from the films that were dried at 80 °C for 24 h. As seen from Figure 2, this temperature is slightly above the T_g of the films with 10−13% Triton. We investigated the time dependence of the crystallinity when annealed at this temperature, with the films with 13% Triton, that were dried only at room temperature for several weeks (set 2). Figure 4 shows the change in heat of fusion with annealing time. It is seen that the as-prepared film shows a modest ΔH of 5 J/g. The maximum ΔH is attained in 24 h. Up to 18 h of annealing, the increase in ΔH is almost linear, at a rate of 0.8 J/(g h). As noted above, the ΔH of 21 J/g obtained here is the same as the maximum ever reported, by annealing at significantly higher temperatures. Thus, Triton enables crystallization at a much lower temperature.

As mentioned in the Introduction, Tsuburaya and Saito[8] reported the crystallization of polycarbonate in blends with PEO. Their studies focused on isothermal crystallization, after melt quenching the sample from 260 °C. The T_g of the blend with 70/30 PC/PEO was reduced to 105 °C. Using crystallization temperatures of 140 or 180 °C, maximum crystallization was achieved in 400 and 100 s, respectively. Their interpretation of the crystallization was based on spinodal decomposition rather than the plasticization effect of PEO. Figure 7 of their paper resembles the optical micrograph shown in Figure 3a, in which the spherulites are clustered in one region. In addition, we found in our case that crystallinity develops only beyond a concentration of 10% Triton X-100. The temperature of annealing (80 °C) was slightly above the T_g of polycarbonate with such concentrations of the surfactant. To verify whether annealing above T_g is the main contributor, a sample with 5% (w/w) Triton X-100 was annealed at 120 °C (above the T_g of 108 °C) for 24 h. Although optical microscopy showed a very small concentration of spherulites, no endotherm could be detected with the DSC. Thus, if there was any crystallinity induced, it is negligibly small. The reduction of the T_g itself does not play a role in crystallization in the case of polycarbonate. For example, when the hole transport molecule TPD is dispersed in polycarbonate, the T_g reduces to about 70 °C, with 50% concentration of the small molecule.[24] Annealing in the range of 120−140 °C causes the phase separation and crystallization of TPD and not the crystallization of polycarbonate. Thus, the crystallization observed here with annealing at 80 °C and a minimum concentration of 11% Triton X-100 can be attributed to a combination of plasticizing effect and the phenomenon similar to that observed by Tsuburaya and Saito.[8]

Conclusions

The surfactant Triton X-100 induces crystallization of polycarbonate with a minimum concentration of 11% by annealing at 80 °C. The crystallinity of the sample with 13% (w/w) Triton as measured by X-ray diffraction is about 18%. This is in the range of crystallinity obtained by annealing or by solvent vapor exposure.[20,25,26] The heat of fusion is in the range of 20 J/g, which is again the maximum recorded[16,27] for samples annealed for several hours at temperatures in the vicinity of 200 °C. Thus, the "ultimate" crystallinity reported so far with various thermal/solvent exposure treatments is achieved here at a lower temperature. It is believed that in addition to the plasticization effect the spinodal decomposition, as in the case of polycarbonate/PEO blends, could also be a contributing factor in the crystallization.

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