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POLYESTERS: PHASE BEHAVIOR IN BINARY BLENDS: AMORPHOUS, CRYSTALLINE, LIQUID CRYSTALS, AND ON TRANSREACTION

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ABSTRACT

Thermal and mechanical studies on several linear polyesters have revealed their behavior in crystalline, liquid crystalline, and amorphous phases. The phase behavior of binary compositions has also been studied by DSC and in combinations including the polycarbonate of bisphenol-A. Regions of amorphous compatibility and incompatibility have been identified. The conditions for transesterification have also been determined and the thermal properties measured for the resultant new polyesters.

INTRODUCTION

During the course of compatibility studies on binary polyester blends, the potential of chemical reactions between components can also be of fundamental and practical importance[1]. In the case of polyester pairs, transesterification is readily facilitated, opening a new route for preparation of novel copolymers with various degrees of randomness and composition[2,3].

The concept of transesterification of polyesters has been previously discussed in detail[1,4]. Application to commercial polymers, however, has only begun recently, partly because of limited industrial development of new polymers. Moreover, as most pairs of polymer blends are incompatible, partially or completely reacted polymer pairs, i.e., block or random copolymers, could well exhibit better properties than the corresponding polymer blends because of the homogenizing effect of new copolymers made by coreaction.

AMORPHOUS BLENDS

This project is devoted to a study of the physical blends and transreacted copolymer products of a polyarylate (PAr) and bisphenol-A polycarbonate (PC). Both polymers are amorphous thermoplastics of relatively high T_g. The PAr is bisphenol-A-terephthanoyl-isophthanoyl (2:1:1) copolyester.

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Physical blends of bisphenol-A polycarbonate (PC) and the polyarylate (PAr) exhibit by thermal analysis two amorphous phases: a pure PC phase and a PAr-rich miscible mixed phase. On controlled thermal treatment, transreaction between PC and PAr takes place mainly in the mixed phase, producing a new copolymer. Reaction progression from block to random copolymers has been traced by DSC, ^{13}C NMR and GPC. The final product of transreaction is an amorphous copolymer showing a single T_g depending on the original binary composition.

BLENDS WITH CRYSTALS

Blends of poly(ethylene terephthalate) (PET) and the copolyester bisphenol-A-terephthaloyl-isophthaloyl (PAr) (2:1:1) have been studied also before and after transesterification. The physical blends exhibit phase separation in their amorphous states: a pure PET phase and a mixed PAr-rich phase. In spite of this phase separation, PET crystallinity in blends, normalized to PET fraction, surprisingly goes through a maximum at 25% PAr content. The transesterified copolymers are noncrystallizable and exhibit a single T_g between those of starting polymers, PET and PAr.

Blends of poly(butylene terephthalate) (PBT) and the copolyester bisphenol-A with 50% terephthalate-50% isophthalate (PAr), also before and after transesterification, have been studied by thermal and dynamic mechanical tests to determine crystallinity and phase behavior. Blends without transesterification, as prepared by solution precipitation, show a single T_g, indicating amorphous miscibility of PBT and PAr. A melting point depression for PBT crystals is not observed; this means PBT crystallizes excluding PAr and that the entropy of melting is small. The highest fractional crystallinity for PBT is obtained at 20-35% of PAr. Transesterified blends were obtained by holding the physical blends at 250°C for up to 16 hours. The transesterified systems show higher T_g's than the corresponding physical blends and also show a marked melting point depression and lesser PBT crystallinity at the corresponding increased PAr content.

Some unusual x-ray diffraction results have been obtained corresponding to an ordered structure in binary blends of a poly(butylene terephthalate) (PBT) with the polyarylate. The polyarylate is a noncrystallizable copolyester, bisphenol-A with a 50-50 mix of terephthaloyl-isophthaloyl units. The two polyesters have been previously found by us to be compatible in their mutual amorphous phase. The x-ray data are shown to be consistent with a nematic order for the PBT in the blends.

The miscibility of bisphenol-A polycarbonate (PC)/poly(ε-caprolactone) (PCL) was investigated with differential scanning calorimetry. A single glass transition was found across the compositional diagram, yet no depression was observed in the melting points of either PC or PCL. A series of PCL-rich blends, crystallized at several temperatures, melted at the same temperature within experimental error. The Hoffman-Weeks extrapolations were linear and identical with that of the PCL homopolymer. The Flory (χ) interaction parameter must thus be zero or slightly positive for these blends. Phase separation prior to crystallization was not the cause of the similar melting endotherms, since the crytallization kinetics follow the expected trend for compatible blends. The PC Hoffman-Weeks extrapolation could not be made, since the blends are reactive at the higher crystallization temperatures required for this component. This reaction was demonstrated by Soxhlet extraction, FTIR and NMR spectroscopies, and turbidimetric titration to be thermooxidative chain branching rather than transesterification between these two condensation polymers.

BLENDS WITH LIQUID CRYSTALS

Many polymer types which exhibit liquid-crystalline properties have been synthesized and examined in the last decade. Among these, thermotropic liquid-crystalline polymers are currently of considerable interest because of their potential applications in, for example, high-strength fibers and films.

Certain aromatic polyesters with rigid backbones are found to be thermotropic liquid crystalline. A specific polyester copolymer, a modified linear poly(ethylene terephthalate) (PET) incorporating a concentration range of the p-oxybenzoate (POB) moiety has been studied extensively and found to show a nematic mesophase. One of these copolymers, containing 60-70 mol % POB units, shows a maximum in mechanical properties which is superior to the corresponding glass-fiber-reinforced PET. Blending such liquid-crystalline copolymers with other polymers could represent an important procedure for industrial application and for fundamental studies of phase behavior and properties. The PET-POB copolymer alone is of interest because it exhibits two amorphous phases: a PET-rich "flexible" phase and a POB-rich "rigid" phase.

The purpose of this first study is to show the phase behavior of a liquid-crystalline copolyester with poly(butylene terephthalate) (PBT).

Binary blends of PBT and a liquid-crystalline copolymer, a PET modified by 60 mol % p-oxybenzoate (POB), are found to be compatible in the "flexible" low-T_g phase of the copolymer, composed mainly of the terephthalate-rich component. Incompatibility was observed by thermal analyses and by dynamic mechanical tests for the "rigid" higher-T_g phase.

The phase behavior for each of two other linear thermotropic liquid crystalline polyesters with a corresponding low molecular weight liquid crystal of similar structure have been investigated. Two distinct types of phase diagrams have been obtained for binary mixtures of a polymer, one containing an in-chain azoxybenzene moiety mixed with para-azoxyanisole and one containing a naphthalene unit mixed with a dimethylester liquid crystal. These phase diagrams were studied by DSC, polarized light microscopy and x-ray diffraction. From this understanding of the physical mixtures a transesterification reaction incorporating the bifunctional low molecular weight liquid crystal by a solid-state reaction into the naphthalene-containing polyester was undertaken. This reaction may be viewed as a potential new processing technique for polymers. The thermal stability of an interreacted blend was shown to be superior to that of either individual component by thermogravimetric analysis. Thus, the potential new processing technique features a lower melting, lower viscosity blend followed by the incorporation of the dimethylester liquid crystal into the polyester main chain producing a more rigid, more stable polymer backbone.

The phase diagram has been obtained for binary blends of two ester thermotropic liquid crystals. They are poly(bisphenol E isophthalate-co-naphthalate) in a para-substituted phenyl ester of terephthalic acid and bis(p-(methoxycarbonyl)phenyl) terephthalate. This binary system exhibits miscibility in a nematic phase and does not form cocrystals. The crystal-to-nematic phase transition has been characterized by the temperature and heat of transition data and by the Flory-Huggins theory for the melting point depression of a polymer-diluent system. From the extrapolated melting point depression data, the heat of fusion of the crystal-nematic phase transition for the polyester is found to be 20.3 ± 0.6 cal/g. The eutectic composition is ~ 24 wt % polymer at 247°C with a eutectic heat of transition of ~ 20 cal/g. The heat of fusion of bis(p-(methoxycarbonyl)phenyl) terephthalate is ~ 30.0 cal/g for the crystal-nematic phase transition. The phase behavior was examined at high copolyester content with three different molecular weights of BPE/I/N20. These blends were subsequently transesterified in the solid state at 220°C, and the changes in phase transitions are reported. The phase behavior and transesterification were characterized by DSC, TGA, polarized light microscopy, x-ray diffraction, and dilute-solution viscometry. The thermodynamic criteria for the melting point depression and the kinetics of transesterification are also reported for the utilization of this new processing technique.

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