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Blends of Polyimides and Their Morphology

Saule Kudaikulova[1], Galina Boiko[1], Bulat Zhubanov[1], N. Ashurov[2], Sh. Sodykov[2], G. Nikonovich[2], S. Rashidova[2] and Marc J.M. Abadie[3]*

[1]Institute of Chemical Sciences, 106 Valihanov, 480100 Almaty, Kazakhstan

[2]Institute of Chemistry and Physics of Polymers, 7b Kodyryi, 700128 Tashkent, Uzbekistan

[3]Montpellier University 2, Science & Technology of Languedoc, Laboratory of Polymer Science & Advanced Organic Materials, Place Eugène Bataillon, 34095 Montpellier CDX 05, France

Abstract

The formulation of macromolecular blends on the basis of polyimides using one step catalytic polycyclocondensation is reported. Polymers with active functional groups (polyacrylamide, polycaproamide) have been suggested as catalysts for the reaction of alicyclic dianhydrides with aromatic diamines in protolytic medium. Films made from macromolecular blends of synthesized polymers have been investigated by X-ray diffractometry and scanning electron microscopy. It has been shown that single step formation of polyimide on the polymer matrix presents the possibility to prepare thin structured disperse blends in comparison with simple mixing of homopolymers.

Introduction

Most of the commercially available plastics, represent mixtures of two or more polymers including special additives. Mixing provides the opportunity to design materials which are characterized by the sum of useful properties of individual component(s). However great majority of polymers are incompatible, which results in phase separation, uncontrolled development of morphology, resulting in poor physical properties of the end-product. Presently, the optimal morphology of polymer blends is achieved by two ways: use of compatibilizers and by reactive mixing of components with functional groups. Creation of polymer blends on the basis polyimides (PI) has several advantages, because of their high thermal and radiation stability. However, some common problems associated with blend formation using Pis are the use of multisteps and low solubility of Pis. New way of solution of this problem is connected with the possibilities, which presents one step polycyclocondensation of alicyclic dianhydrides with aromatic diamines in protolytic medium – formulation of polymer blend by catalytic synthesis of polyimide on polymer matrix (P2). Previously it was shown that different organic compounds such as carboxylic acids [1] and tertiary amines [2] were efficient catalysts of one step high temperature synthesis of PI on the basis of alicyclic dianhydrides and aromatic diamines in protolytic solvents. The process accelerates both the steps during PI formation: polyacylation and imidization. Along with acceleration of polyacylation step, it also helps in shifting the equilibrium of the first step by conversion of polyamic acid into polyimide [3]. Significant increase of rate constants of the polyacylation step leads to increase in molecular weights of final PI. In this report, we discuss reactive preparation of polyimide-polyamide blends and study of their morphology.

Experimental

Reagents

Anhydrides of alicyclic tetracarboxylic acids have been prepared in the Laboratory of Polymer Synthesis of the Institute of Chemical Sciences, Kazakhstan. Synthesis was carried out making use of Diels-Alder reaction of maleic anhydride with benzene or toluene, in excess of aromatic reagent in the presence of acetophenone as sensitizer, under UV-irradiation [4].

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*corresponding author. E-mail: abadie@univ-montp2.fr

The dianhydrides thus obtained was repeatedly rinsed with hot acetone. The dianhydrides were boiled with 1.5% excess of acetic anhydride, washed with diethyl ether and dried at 100°C under vacuum until constant weight. The dianhydrides were finally sublimed as the last step of purification.

Dianhydride of tricyclo-[4.2.2.02,5]-dec-7-en-3,4.9.10-tetracarboxylic acid (BA – adduct of benzene and maleic anhydride). Elemental analysis: calculated: C 61.31; H 3.66; found C 61.11; H 3.61; M.P.: 3.510C; neutralization equivalent: calculated 137.0; found 137,0.

Oxydianiline (ODA) was sublimed under vacuum at 200°C/6×10^{-3} mm Hg; m.p.: 185.6°C.

Acrylamide was recrystallized from benzene three times.M.p.84-85°C.

Polyacrylamide was prepared by radical polymerization of 10% aqueous solution of monomer in presence of $(NH_4)_2S_2O_8$. Obtained polymer was analyzed with respect to unreacted monomer by bromide-bromate method. Intrinsic viscosity [η] in water at 25°C = 0.82 dl/g, M_n = 46600.

ε-caprolactame was distilled at reduced pressure, B.P. 139°C/12 mm Hg, M.P. 68-69°C.

Poly-ε-caproamide was twicely deposited from cresol solution into alcohol, extracted by ethyl alcohol. Intrinsic viscosity [η] in m-cresol at 25°C is 0.8 dl/g, M_n = 80000.

The solvents, benzene, m-cresol, dimethylsulfoxide (DMSO) were purified by usual methods.

Synthesis of polyimides

PIs have been synthesized by one step polycyclocondensation of dianhydride (BA) with ODA in m-cresol in the presence of polyamide at 170-190°C in the inert atmosphere. The final product – polyimide-polyamide blend was poured into acetone and dried under vacuum at 100°C. Composite solutions in m-cresol were cast on the glass plate and dried in an oven, while raising the temperature gradually from 100 to 180°C.

Isolation of water in the course of one step synthesis was investigated by dynamic aquametry by modified Fisher's reagent [5].

The reduced and intrinsic viscosity of the polymers were determined in DMSO at 20°C, concentration of the solution 0.5 dl/g, by using an Ubbelhode viscometer.

Molecular weights of PI samples were determined by Archibald method using the ultracentrifuge (MOM G-120) at 20°C and rotation of 20 000 revolutions/min.

The intrinsic viscosity [η] measurements in DMSO solutions of the polymer fractions with determined molecular weights allowed to find hydrodynamic constants: a = 0.61 and k = 9.77.10^{-4}.

Infrared spectra were recorded on specord "Jasco IR-180", using KBr pellets or polymer films of 4-6 μm thickness. The spectrum is characterized by presence of the bands: ν = 1380; 1720, 1780 cm^{-1} related to absorption of C–N; C=O of the imide functions, respectively.

Thermogravimetric analysis (TGA) was performed on derivatograph Q-100 (System Paulic, Paulic Erdey) MOM, at heating rate 10°C/min.

X-ray analysis was performed on X-ray diffractometer (DRON-2).

Scanning electron microscopy investigations were carried out on "TESLA" microscope.

Results and Discussion

Reaction of alicyclic dianhydrides with aromatic diamines in the presence of definite quantities of polymer matrix (P2) is conducted by one step high temperature polycondensation according to the following scheme:

$$\text{dianhydride} + \text{diamine} \xrightarrow[\text{P2}]{\text{m - cresol, 180°C}} \{\text{polyamic acid}\} \longrightarrow \text{polyimide blend (PI/P2)}$$

Two types of polymers with amide functional groups as polymer matrix (P2) are studied: amide groups in main chain (polyamide 6 - PA6) and as side groups (polyacrylamide - PAA). IR spectra of formed PI are characterized by the presence of 1720, 1780, 1380 cm^{-1} vibration bands. Investigation of the effect of the nature of polymer matrix (P2) under similar experimental conditions, have been carried out with corresponding monomer form.

Investigation of the kinetics of the formation of PI reaction was carried out by adapted Fisher's method [5], the results of which are presented in Table

1. It is evident that acrylamide and polyacrylamide display the role of catalysts during the formation of PI. Further, the addition of acrylamide and polyacrylamide into reactive mixture of monomers accelerates both steps of PI formation: polyacylation (k_1) and imidization (k_2). It is also obvious from these data that polymer form of catalyst is more efficient than the monomeric counterpart.

Table 1

Kinetic parameters of the reaction of BA with ODA

T°C	Without catalyst		Polyacrylamide		Acrylamide	
	$k_1\times10^3$, 1/mol×s	$k_2\times10^3$, s^{-1}	$k_1\times10^3$, 1/mol×s	$k_2\times10^3$, s^{-1}	$k_1\times10^3$, 1/mol×s	$k_2\times10^3$, s^{-1}
175	8.17	1.32	14.70	1.95	10.55	1.57
180	9.00	1.53	15.70	2.17	–	–
185	10.20	1.80	16.70	2.42	–	–
190	11.00	2.05	18.20	2.58	–	–
E, kJ/mol	35 ± 2	51 ± 1	24 ± 1	33 ± 1	–	–

Synthesized polymer blends PI/P2 are soluble in DMSO. The molecular weights of the PIs depend on a number of factors: temperature and duration of synthesis, concentration of monomers and catalyst. Molecular weights of PI were determined from changes of reduced viscosity of PI solutions in DMSO at 20°C, after extraction of P2 component from the blend. Determination of optimal conditions for the PI synthesis in the presence of PA6, was carried out by sequential variation of any one parameter and establishing the dependence of reduced viscosity on the said parameter.

Dependence of reduced viscosity of synthesized PI on duration of the process clearly demonstrates catalytic efficiency of P2 matrix: along with the increase of final value of PI molecular weight the increase of the rate of it's achievement is also evident (Fig. 1).

Investigation of the temperature dependence (Fig. 2) has shown that the use of polymer catalyst allows the reaction to proceed under mild conditions.

An interesting observation has been the dependence of molecular weight of PI on the concentration of polymer as the catalyst. It is observed that the concentration dependence curves for the polymer form of catalyst have limited character whereas the effect is extreme for the monomer (Fig. 3). A probable explanation of such effect is that the polymer matrix forms compact globules and as a result part of the functional groups are placed within the glob-

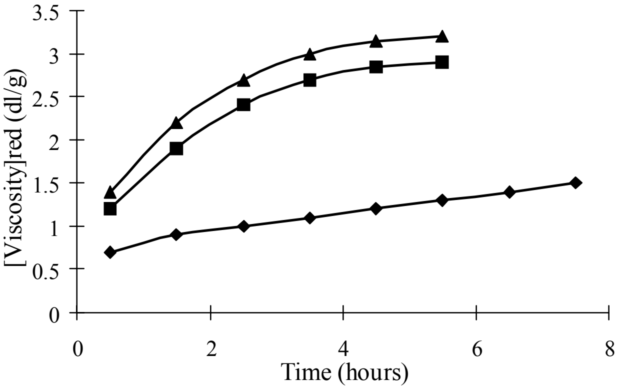

Fig. 1. Dependence of reduced viscosity of polyimides on duration of synthesis – ε-caprolactame (□), polycaprolactame (Δ), without catalyst (◊)

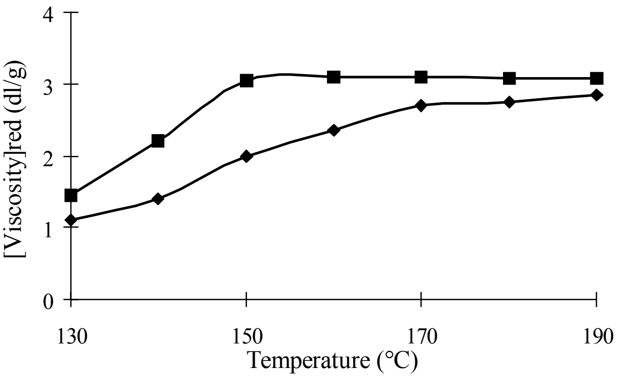

Fig. 2. Dependence of reduced viscosity of polyimide on the temperature of the reaction ε-caprolactame (◊), polycaprolactame (□).

ule and the reaction is catalyzed by functional groups situated on the surface of the globule.

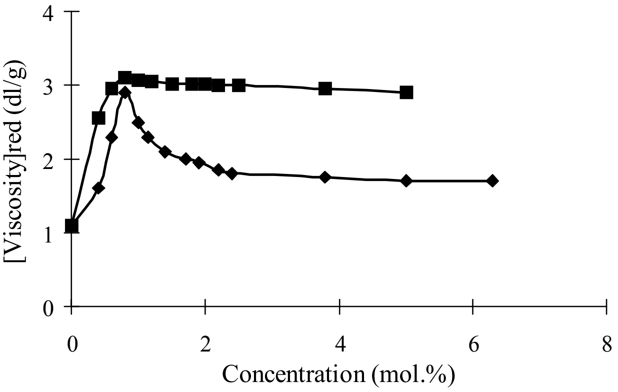

Fig. 3. Dependence of reduced viscosity of polyimide on the concentration of catalyst – ε-caprolactame (◊), polycaprolactame (□).

Optimal conditions of synthesis are presented in the Table 2.

Previously conducted investigations [2] of mechanism of the reaction suggested that catalytic action of tertiary amines is due to the formation of triple complex: catalyst-m-cresol-dianhydride, which results in increase of reactivity of anhydride groups. In case of the polymer catalyst, it may be suggested that molecules of dianhydrides orient with functional groups of polyamide matrix in definite way with formation of reactive complexes. Polycondensation of these reactive complexes is run directionally along macromolecular chain of polymer catalyst. This reasoning is supported by the fact that an increase in molecular weight of the polymer catalyst at constant concentration leads to an increase in the molecular weight of final PI. The results are presented in the Table 2.

Limited character of the relation between reduced viscosity and concentration of polyamide matrix (Fig. 2) allows one to formulate polymer blends with high content of polyamide matrix. Preference of PA6 matrix is due to close resemblance of thermal and mechanical properties to alicyclic PI.

The study of micromorphology, fine and supermolecular structure of composites at different formulations was investigated by scanning electron microscopy. It is observed that PI film is absolutely nonstructured, with smooth surface, it does not shine in crossed nicols and there are no other supermolecular formations. General morphology of PI/PA6 blends with different ratios of the components represents PI matrix composed from small round particles with the size within 0.1-15 μm, the size of last ones increase with the content of PA6. At greater magnifications, it is clearly seen that each particle in it's turn is not homogeneous and represents itself similarity of drop which include in smaller particles (<1 μm). In addition polyamide phase appears as oblong interface of PI drops. These particles are discrete with the size not larger than 1 μm. Polyamide phase shines in polarized light with the intensity depending on the concentration and molecular weight of PA6. This is connected with better crystallization of high molecular PA6.

Another picture is observed with the mixing of ready components: high molecular PI and PA through common solvent. In this case morphology of the film is characterized by homogeneous PI matrix with uniform distribution of PA6 phase with the size of particles 1-50 μm. Increase of PA6 content in the blend up to 80% results in the phase inversion and the micrograph shows large scale spherulite structure of PA matrix with incorporation of small PI particles.

Stabilization of morphology of PI/PA6 blend is

Table 2

Optimal conditions and main characteristics of PI obtained in the presence of different catalysts

No	Catalyst	Optimal conditions		[η], dl/g	M×10^{-5}
		C_{mon}, wt.%/duration, hours	C_{cat}, mol.%/T°C		
1	Acrylamide	35/4	0.5/180	2.12	2.95
2	Polyacrylamide	30/4	0.5/150	2.18	3.09
3	ε-caprolactame	35/4	0.5/180	2.08	2.86
4	Polycaproamide	30/4	0.5/150	2.15	3.02

due to the formation of compatibilizing structures of different types, which stabilize the size of disperse phase. Interaction of terminal carboxyl and amine groups of PA6 with anhydride and amine groups of PI can lead to formation of disperse phase with wider distribution of particles by the size. X-ray diffraction analysis (Fig. 4) shows that PA6 crystallizes into α- and γ-modifications (1), PI forms ordered structure (2) similar to liquid crystal polymers.

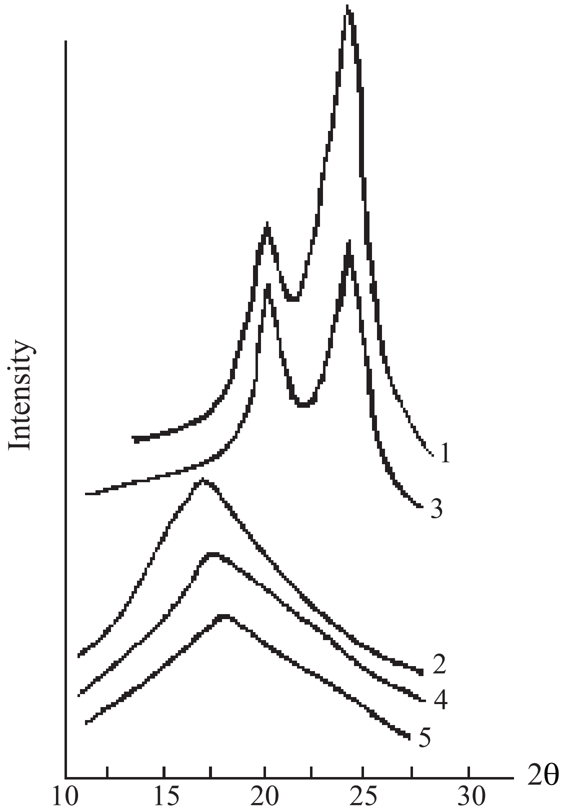

Fig. 4. X-ray diffractograms of the samples: PA6 – 1; PI – 2; PI/PA blend (20:80) – 3; synthesized composite PI/PA6 (35:65) – 4; (15:85) – 5.

Introduction of PA6 into PI results in significant decrease of order regulation of PI, though PA6 itself does not appear (4, 5). Apparently this is due to steric hindrance of PA6 crystallization under the conditions of composite formation. Possible crystal phase of PA6 observed by microscopic methods is formulated by defect nonperfect crystallization. Theses are only observed clearly with high content of PA6 in the composition (3) (main diffraction maximums at 2θ = 21.2° and 24.0° inherent to a-cristall modification of PA6). The observed phenomenon is confirmed by derivatograph analysis (Fig. 5).

It is evident that melting point for PA6 in the composition has been lowered to 200°C (initial M.P. for PA6 is 215°C), which apparently, is associated with nonperfection of crystallites.

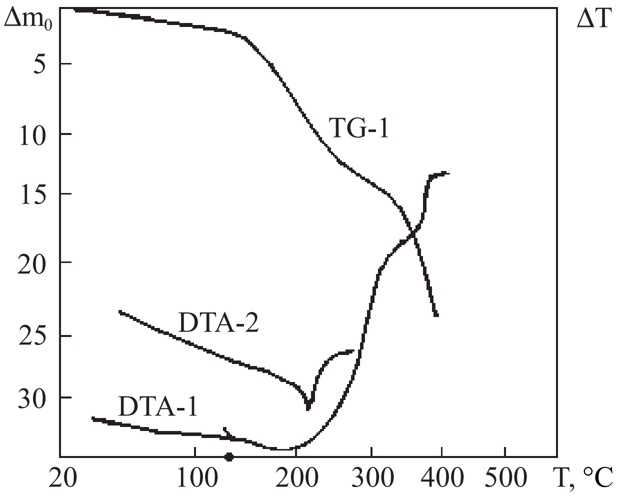

Fig. 5. The curves of differential thermal analysis and thermogravimetric analysis of the sample synthesized PI/PA6 (35:65) – 1 and fragment of DTA for PA6.

Conclusions

Our studies show that PI/PA6 blend obtained from common solvent represents an incompatible system, which leads to microseparation and formation of the films with heterogeneous structure. However, progressive increase in the molecular weights of PI component in the course of one step catalytic synthesis in the bulk of reactive mixture, lowers the incompatibility and results in the formation of disperse PI/P2 system with definite morphology. The details of the fine structure of these films are determined in relation to components, type of polyamide, it's molecular weight and a number of other factors which are presently under investigation. The results from the present investigation shows that the upper limit of disperse phase particles size and their uniform distribution in the bulk of composite films, are appropriate parameters to optimize the conditions of reactive formulation.

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