

Influence of Azobenzene Units on Imidization Kinetic of Novel Poly(ester amic acid)s and Polymers Properties Before and After Cyclodehydration

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ABSTRACT: In this article, the imidization reaction kinetic of novel poly(ester amic acid)s with azobenzene units as side groups was studied by dynamic experiments by means of differential scanning calorimetry. Polymers differ in the number of chromophore moieties in their repeating unit and position in which azobenzene group is attached to the polymer chain. The kinetic parameters of poly(ester amic acid)s conversion to poly(ester imide)s was compared with data calculated for parent polymer, that is, without azobenzene groups. For the first time to our knowledge, the imidization kinetic of polymers with side azobenzene groups was studied. Kinetic parameters, such as the activation energy and frequency factor were estimated with the by Ozawa model [(E(O) and A(O)), respectively] and Kissinger model [(E(K) and A(K), respectively)].

The values of activation energy determined with both models were in the range 167.1–198.3 kJ/mol. The lowest activation energy of imidization reaction exhibited polymer in which azobenzene units were placed between amide linkages. Polymers were characterized by FTIR, ¹H-NMR, X-ray, and UV–vis methods. The glass transition temperature of resultant poly(ester imide)s was in the range of 217–237°C. The presence of chromophore units slightly decreased T_g and significantly improved their solubility and optical properties. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 2624–2633, 2010

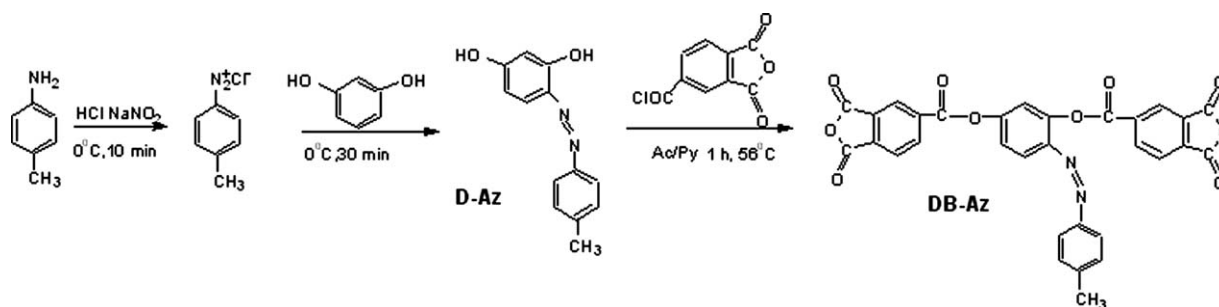
Key words: azo polymers; polyimides; differential scanning calorimetry; activation energy; Ozawa and Kissinger models

INTRODUCTION

Aromatic polyimides (PIs) play a key role as materials for many applications ranging from dielectric films for the electronic industry and orientation layers liquid crystal industry, lightweight load-bearing heat-resistant composites and adhesives for the aerospace industry, to gas-separation membranes due to their outstanding thermal, mechanical, electrical, and chemical resistance properties.^{1,2} Such performances have inspired many researchers to modify, study, and use PIs in the field of optoelectronics and photonics. PIs, mainly with covalently bonded azobenzene derivatives, have been attracting attention in design optic (NLO) polymers, namely with respect to their second-order NLO phenomena^{3–7} and their third-order NLO properties suitable for optical data storage were investigated.^{8–15} In the classical method of PI synthesis, a two-step method is generally used, that is, a tetracarboxylic acid dianhydride with diamine generate a poly(amic acid),

which is then imidized (cyclodehydrated) to the corresponding PI by extending heating at elevated temperatures or by treatment with chemical dehydrating agents. The most widely used second step in the two-step method of poly(amic acid) synthesis involves thermal imidization (250–400°C) in the solid state. The degree of imidization determining PIs physical properties. Knowledge of the thermal imidization kinetics permits controlling the degree of conversion achieved after a schedule. Moreover, in NLO poly(amic acid)s the imidization temperature should be carefully applied to avoid destruction of some chromophores that can be unstable in such process.¹⁶ Therefore, it is important to verify the imidization kinetics for photonic and optoelectronic applications especially of chromophore containing PIs. There are several techniques to monitor the imidization process such as infrared spectroscopy (IR), UV spectroscopy, fluorescence, and differential scanning calorimetry (DSC).¹⁷ The most powerful method is DSC because the imidization reaction of PAA to PI is highly endothermic. There are two DSC methods for investigation of curing process, that is, isothermal and dynamic measurements. The advantage of isothermal experiments is that the rate constants at each temperature are better defined and the constants obtained at different temperatures

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Scheme 1 Synthetic route of DB-Az.

permit determination of the activation energy associated with the cure reactions.^{18,19} On the other hand, the nature of the reactions and the final products may differ at different temperatures, and the kinetic parameters thus obtained are without ambiguity.²⁰ Dynamic experiments conducted at a specified heating rate by means of DSC will yield conversion-time-temperature data that are comprehensive enough to allow direct evaluations of the kinetic parameters. In comparison with the isothermal method, the dynamic cure is theoretically more difficult because of the complex temperature dependence of the rate constant and the peculiar feature of the cure, although it is a case, which more closely simulates the process.²¹ A single dynamic run gives much information than several isothermal runs. Dynamic measurements can provide kinetic information over a larger temperature range and there are not pre-cure problems, as with isothermal experiments in which the sample must first be heated to the isothermal hold temperature, during which cure reactions may take place. Dynamic measurement is valuable as an initial method to isothermal studies and is important for analyzing the cure kinetics of systems with multiple exotherms.²²

In this study, the dynamic DSC experiments were carried out to investigate the conversion of novel poly(ester amic acid)s (PAA) with azobenzene units as side groups to corresponding poly(esterimide)s (PESI). In this work, the experimental DSC results were analyzed by Ozawa and Kissinger models.^{22,23–30} These methods, in which the system is cured on various heating rates, are simple and valuable for the study of cure kinetics. The objective of this work were (1) the determination of the activation energy (E) and the frequency factor (A) of reaction imidization of novel PAA with azobenzene moieties, (2) comparison of the kinetic parameters estimated by different models, and (3) investigation of chosen polymer properties important for further applications such as: solubility, thermal, and optical properties. For the first time to our knowledge, the imidization kinetic of polymers with side azobenzene groups was studied.

EXPERIMENTAL

Materials

Trimellitic anhydride chloride (TMACl), *N*-methyl-2-pyrrolidone (NMP) anhydrous, tetrahydrofuran (THF), dimethylformamide (DMF), dimethylsulfoxide (DMSO), methanol, 1,3-phenylenediamine, resorcin, *p*-toluidine, sodium acetate anhydrous, acetic anhydride, acetic acid, hydrochloric acid, and other necessary starting chemicals were purchased from Aldrich Chemical and were used as received. Acetone, pyridine, and *m*-cresol were purified by distillation in the usual manner. 2,4-Diamine-4'-methylazobenzene and dianhydride without azobenzene group were prepared as reported in our previous papers.^{13,31} The newly synthesized diesterdianhydride with azobenzene group (**DB-Az**) was obtained as reported in our article for different dianhydride (Scheme 1).³² The synthesis of **DB-Az** consisted of two parts: in the first one *p*-toluidine was converted to the diazonium salt, which was subjected to coupling reaction with resorcin to give 2,4-dihydroxy-4'-methylazobenzene (**D-Az**). In the second one **D-Az** was subjected to the condensation reaction with TMACl to obtain **DB-Az** (Scheme 1).

Synthesis of 2,4-dihydroxy-4'-methylazobenzene (**D-Az**)

To 20 mmol of *p*-toluidine 5.4 mL of concentrated hydrochloric acid and 20 mL of water were added. The mixture was placed in the ice bath. To the cooled mixture, a solution of 20 mmol of sodium nitrite in 3 mL of water was added dropwise and the resulting solution was stirred at a temperature between 0 and 5°C within 15 min. Then, the solution containing 20 mmol of resorcin in 11 mL of methanol was added dropwise. The reaction was carried out for 30 min and was neutralized with sodium acetate. After the temperature was raised to room temperature, the mixture was stirred for 1 h. The product was filtered, washed with large amount of water and dried under vacuum at 70°C (yield: 70%). m.p. 184°C.

D-Az: $^1\text{H-NMR}$ ($\text{DMSO-}d_6$, δ , ppm): 2.35 (s, CH_3 , 3H), 6.35 (s, ArH, 1H), 6.48 (d, ArH, 1H), 7.33 (d, ArH, 2H), 7.65 (d, ArH, 1H), 7.73 (d, ArH, 2H), 10.50 (s, ArOH, 1H), 12.48 (s, ArOH, 1H); FTIR (KBr, cm^{-1}): 3298 (OH), 1620, 1592.

Synthesis of diesterdianhydride

DB-Az: To a 100 mL flask equipped with magnetic stirrer, condenser and dropping funnel was charged 22 mmol of trimellitic anhydride chloride (TMACI) and 25 mL of dry acetone. After the mixture was heated under reflux, a solution of 10 mmol of **D-Az** and 22 mmol of dry pyridine in 25 mL of acetone was added dropwise for 30 min. The mixture was stirred and heated under reflux for 1 h. After cooling to room temperature, the resulting precipitate was filtered off and washed with methanol and then dried in 60°C . The crude product was washed with acetic anhydride and dried in vacuum at 150°C (yield: 40%). m.p. 261°C , UV-vis (NMP): $\lambda_{\text{max}} = 346$ nm.

DB-Az: $^1\text{H-NMR}$ ($\text{DMSO-}d_6$, δ , ppm): 2.33 (s, CH_3 , 3H), 7.29 (d, ArH, 2H), 7.55 (d, ArH, 2H), 7.58 (d, ArH, 1H), 7.62 (d, ArH, 1H), 7.83 (d, ArH, 2H), 7.95 (s, ArH, 1H), 7.98 (s, ArH, 1H), 8.30 (d, ArH, 2H), 8.33 (s, ArH, 1H), 8.66–8.71 (m, ArH, 4H); FTIR (KBr, cm^{-1}): 1855, 1778 (C=O in anhydride), 1741 (C=O in ester), 2922 (CH_3).

Synthesis of polymers

Synthesis of poly(ester amic acid)s (PAA-X)

Two mmol of diamine was added into a flask and dissolved in 4.9 mL of NMP. Then the flask was put into a cooling bath and 2 mmol of dianhydride was added. Mixture was stirring for 5 h under nitrogen flow. Poly(ester amic acid)s were precipitated in methanol washed and dried in 30°C on vacuum.

PAA-1: $^1\text{H-NMR}$ ($\text{DMSO-}d_6$, δ , ppm): 7.36–7.47 (m, ArH, 3H), 7.61 (t, ArH, 1H), 7.77 (d, ArH, 1H), 8.04 (d, ArH, 1H), 8.24 (t, ArH, 1H), 8.36 (d, ArH, 1H), 8.57 (s, ArH, 1H), 10.59 (d, NH, 1H) 12.5–13.2 (s, COOH, 1H); FTIR (KBr, cm^{-1}): 3342 (NH, OH), 2616 (CH_3), 1737, 1660, 1547 (amide), 743 (C–N bending).

PAA-2: $^1\text{H-NMR}$ ($\text{DMSO-}d_6$, δ , ppm): 2.37 (t, CH_3 , 3H), 7.20 (d, ArH, 1H), 7.36 (m, ArH, 4H), 7.50 (t, ArH, 1H), 7.81 (m, ArH, 4H), 8.03 (t, ArH, 1H), 8.32 (s, ArH, 2H), 8.41 (s, ArH, 1H), 8.60 (s, ArH, 1H), 8.67 (s, ArH, 1H), 8.73 (s, ArH, 1H), 11.03 (d, NH, 1H) 13–14 (s, COOH, 1H); FTIR (KBr, cm^{-1}): 3340 (NH, OH), 2620 (CH_3), 1738, 1661, 1522 (amide), 742 (C–N bending).

PAA-3: $^1\text{H-NMR}$ ($\text{DMSO-}d_6$, δ , ppm): 7.36–7.47 (m, CH, 3H), 7.61 (t, CH, 1H), 7.77 (d, CH, 1H), 8.04 (d, CH, 1H), 8.24 (t, CH, 1H), 8.36 (d, CH, 1H), 8.57

(s, CH, 1H), 10.61 (d, NH, 1H); FTIR (KBr, cm^{-1}): 3342 (NH, OH), 2619 (CH_3), 1741, 1662, 1548 (amide), 743 (C–N bending).

PAA-4: $^1\text{H-NMR}$ ($\text{DMSO-}d_6$, δ , ppm): 2.33 (m, CH_3 , 6H), 7.29 (d, ArH, 3H), 7.51–7.60 (m, ArH, 2H), 7.74–7.94 (m, ArH, 10H), 8.11 (s, ArH, 2H), 8.46 (s, ArH, 2H), 8.66 (s, ArH, 1H), 11.06 (d, NH, 1H) 13–14 (s, COOH, 1H); FTIR (KBr, cm^{-1}): 3339 (NH, OH), 2621 (CH_3), 1736, 1678, 1523 (amide), 739 (C–N bending).

Synthesis of poly(ester imide)s (PESI-X)

Poly(ester imide)s were synthesized by thermal imidization of poly(ester amic acid)s using cyclization conditions established from DSC investigations. Solution of poly(ester amic acid)s in NMP were casted on a glass substrate. Then films were heated up to 210 – 230°C and hold in for 3 h with agreement of half life obtained by DSC method.

PESI-1: $^1\text{H-NMR}$ ($\text{DMSO-}d_6$, δ , ppm): 7.14 (d, ArH, 1H), 7.42 (t, ArH, 1H), 7.47 (s, ArH, 1H), 7.54 (s, ArH, 2H), 7.60–7.66 (m, ArH, 4H), 7.70–7.76 (m, ArH, 3H), 8.18 (t, ArH, 2H), 9.94 (s, NH, 1H); FTIR (KBr, cm^{-1}): 2968 (CH_3), 1778, 1724 (C=O, imide stretching), 1359 (C–N stretching), 745 (imide ring deformation).

PESI-2: $^1\text{H-NMR}$ ($\text{DMSO-}d_6$, δ , ppm): 2.12–2.42 (m, CH_3 , 3H), 7.32 (t, ArH, 2H), 7.37 (d, ArH, 2H), 7.57–7.64 (m, ArH, 3H), 7.81 (d, ArH, 1H), 7.96–8.01 (m, ArH, 1H), 8.21 (d, ArH, 1H), 8.47 (s, ArH, 1H), 8.53–8.65 (m, ArH, 3H); FTIR (KBr, cm^{-1}): 2956 (CH_3), 1784, 1728 (C=O, imide), 1365 (C–N imide stretching), 721 (imide ring deformation).

PESI-3: $^1\text{H-NMR}$ ($\text{DMSO-}d_6$, δ , ppm): 2.06–2.36 (m, CH_3 , 3H), 7.15–7.23 (m, ArH, 2H), 7.29 (d, ArH, 1H), 7.45 (t, ArH, 2H), 7.59 (d, ArH, 2H), 7.73–7.81 (m, ArH, 2H), 7.96 (d, ArH, 1H), 8.17–8.22 (m, ArH, 2H), 8.35 (s, ArH, 1H), 8.57 (d, ArH, 2H), 8.64–8.68 (m, ArH, 2H); FTIR (KBr, cm^{-1}): 2960 (CH_3), 1780, 1724 (C=O, imide), 1366 (C–N imide stretching), 719 (imide ring deformation).

PESI-4: $^1\text{H-NMR}$ ($\text{DMSO-}d_6$, δ , ppm): 2.23–2.48 (m, CH_3 , 6H), 7.27–7.36 (m, ArH, 3H), 7.42 (d, ArH, 1H), 7.58 (d, ArH, 3H), 7.76–7.99 (m, ArH, 6H), 8.25–8.27 (m, ArH, 3H), 8.48 (s, ArH, 1H), 8.60–8.67 (m, ArH, 3H) FTIR (KBr, cm^{-1}): 2956 (CH_3), 1784, 1728 (C=O, imide), 1363 (C–N imide stretching), 723 (imide ring deformation).

Measurements

$^1\text{H-NMR}$ spectra were recorded on a Varian UNITY Inova 300 spectrometer ($\text{DMSO-}d_6$ solvent). Infrared spectra were acquired on DIGILAB (BIO-RAD) FTS 40 A Fourier transform infrared spectrometer Samples were analyzed as KBr pressed pellets. UV-Vis

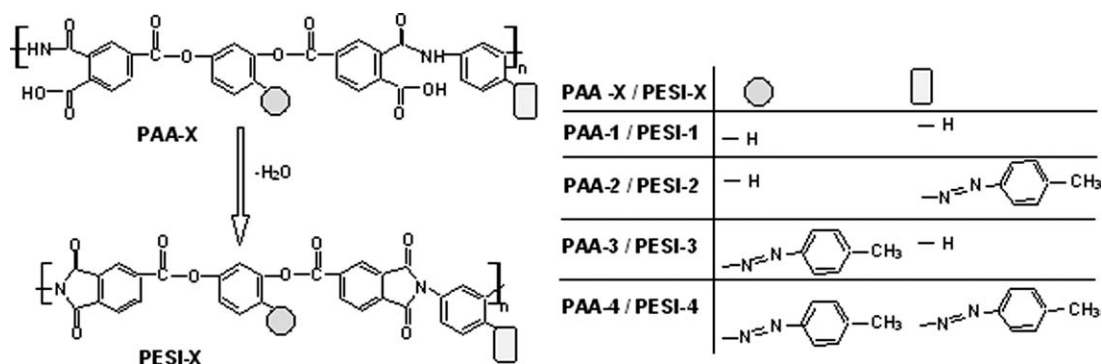


Figure 1 Chemical structures of synthesized polymers PAA-X and PESI-X.

spectra were recorded using a JASCO V570 UV-V-NIR spectrometer. The X-ray diffraction pattern of a solid sample has been recorded using $\text{CuK}\alpha$ radiation on a wide-angle HZG-4 diffractometer working in the typical Bragg geometry.

DSC measurements

DSC measurements were taken with a TA DSC 2010 apparatus (TA Instruments, New Castle, DE). Imidization experiments were performed at heating rates of 10, 15, 20, 30, and 40°C/min in the temperature range of 20–350°C. The glass transition temperatures (T_g) of poly(ester imide)s were determined at heating rate 20°C/min. In this study, T_g was taken as the midpoint of the step-transition. Samples of 5–10 mg in crimped aluminum cell were heated in the DSC apparatus under nitrogen atmosphere (flow = 50 mL/min). An empty cell was used as the reference. The instrument was calibrated with high purity indium.

RESULTS AND DISCUSSION

The imidization reaction of novel synthesized poly(ester amic acid)s (PAA-X) to corresponding poly(ester imide)s (PESI-X) was studied by dynamic DSC measurements. The chemical structures of the investigated polymers are shown in Figure 1.

Polymers differ in the number of chromophore moieties in their repeating unit and position in which azobenzene group is attached to the polymer chain. The kinetic parameters of poly(ester amic acid)s conversion to poly(ester imide)s and their properties were compared with data estimated for parent polymer, that is, without azobenzene groups (PAA-1).

Formation of poly(amic acid)s from dianhydride and diamines process *via* nucleophilic substitution on the anhydride carbonyl atom, with the amine acting as a nucleophile.³³ Therefore, the reaction rate is strongly dependent on the basicity of the amine, the electrophilicity of the anhydride carbonyl, and the

basicity of the solvent. The thermal imidization of poly(amic acid)s involves cyclization through a nucleophilic attack on the acid carbonyl carbon by the free electron pair of the amide nitrogen.³⁴ Although two groups, CONH and COOH, are involved in imidization, this reaction should be treated as first-order, since these groups belong to the same fragment of poly(amic acid), and interaction of the groups with different macromolecules is practically impossible, especially in the solid state.³⁴ A first-order kinetic equation was almost exclusively used to treat imidization kinetics.³⁵ In this study the kinetic of thermal imidization of a poly(ester amic acid)s was investigated in solid state in the temperature range of 100–300°C. The use of the solid poly(ester amic acid)s to investigate imidization kinetics let to remove the complex effect of solvent on imidization. Two different models, that is, Ozawa and Kissinger were chosen to analyze experimental results of the imidization reaction. The advantage of these models includes simplicity and accuracy for various types of cure reactions to estimate the activation energy (E) and frequency factor (A).^{24,26}

Analysis of the DSC results with the Ozawa and Kissinger methods

In this method, the relationships between the heating rates (ϕ) values and the peak endotherm temperature (T_p) values were used to determine the reaction kinetics. Under the assumption that the chemical conversion was constant at T_p and independent of the heating rate, the activation energy (E) was calculated from the Ozawa equation^{26,27}

$$E = -R/1.052 \times \Delta \ln \phi / \Delta (1/T_p) \quad (1)$$

where R is the universal gas constant. The equations derived by Kissinger for E and A are as follows.^{24,29}

$$-E/R = d[\ln(\phi/T_p^2)]/d(1/T_p) \quad (2)$$

$$A = \phi E \exp(E/RT_p)/RT_p^2 \quad (3)$$

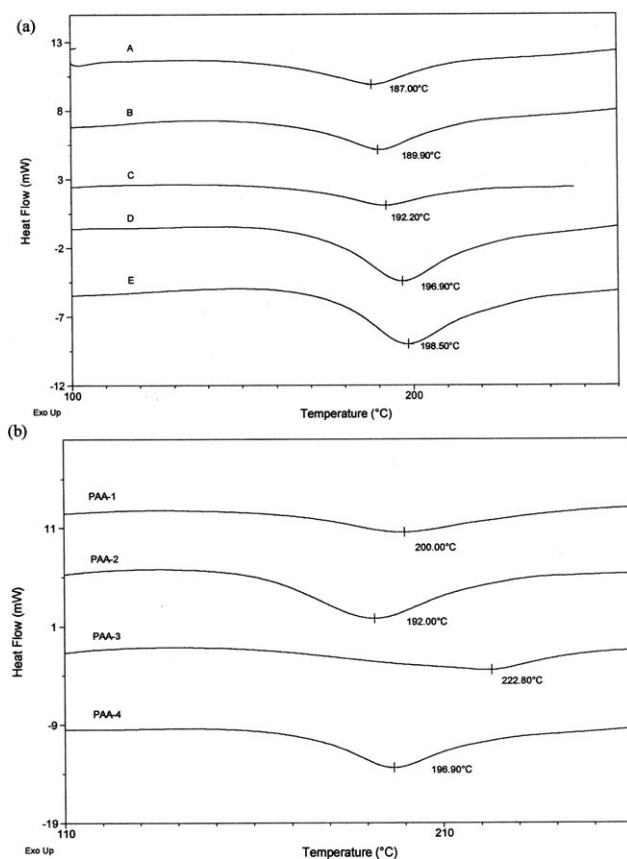


Figure 2 DSC curves for PAA-4 at different heating rates: 10°C/min (A), 15°C/min (B), 20°C/min (C), 30°C/min (D), 40°C/min (E), (a) and at heating rate 30°C/min for all PAA (b).

These methods are simple and convenient in comparison with the cut-and-weigh method and spectroscopic method,³⁰ and the Ozawa and Kissinger methods are independent of sample size.²⁷ Typical dynamic DSC curves at five heating rates for exemplary polymer PAA-4 and for all polymers (PAA-1-PAA-4) at one heating rate are shown in Figure 2(a,b), respectively.

The thermograms present one endotherm due to endothermic imidization reaction. Values of endothermic peaks representing the temperature of maximum imidization rate increased gradually with the heating rate increasing in all investigated poly(ester amic acid)s. At the same heating rates, the position of endothermic peak maximum is depending on polymer structure [cf. Fig. 2(b)]. Introduction of azobenzene units between ester groups (PAA-3) shifted T_p position to the highest temperature compared with polymer without azobenzene units (PAA-1). Whereas, when azobenzene moieties were placed between amide linkages (PAA-2 and PAA-4) which shifted T_p to lower temperatures in comparison with PAA-1 and PAA-3. The imidization reactions for all samples can be safely completed below 250°C with-

out decomposition during cyclodehydration. The subsequent heating after cooling these samples from 250°C showed no traces of an endotherm, indicating that imidization reaction was completed during the dynamic DSC scan.

A plot of $1/T_p$ versus $\ln \phi$ according to eq. (1) (Ozawa model) for each polymer is presented in Figure 3(a). The calculated slope is -0.0413 for PAA-1, -0.0473 for PAA-2, -0.0404 for PAA-3, and -0.0399 for PAA-4. Figure 3(b) shows plots of $\ln(\phi/T_p^2)$ versus $1/T_p$ obtained according to eq. (2) (Kissinger method) for each polymer. Here, the slope is $-23,05$ for PAA-1, $-20,198$ for PAA-2, $-23,633$ for PAA-3, and $-23,85$ for PAA-4.

Figure 4 illustrates the plot for the eq. (3) with E values estimated by the Ozawa and Kissinger models for all PAA-X.

The calculated kinetics parameters, that is, E and A , for poly(ester amic acid)s estimated by the Ozawa and Kissinger models and reaction enthalpy (ΔH) are collected in Table I.

The enthalpy for the imidization was obtained from the integration between the onset and endpoint

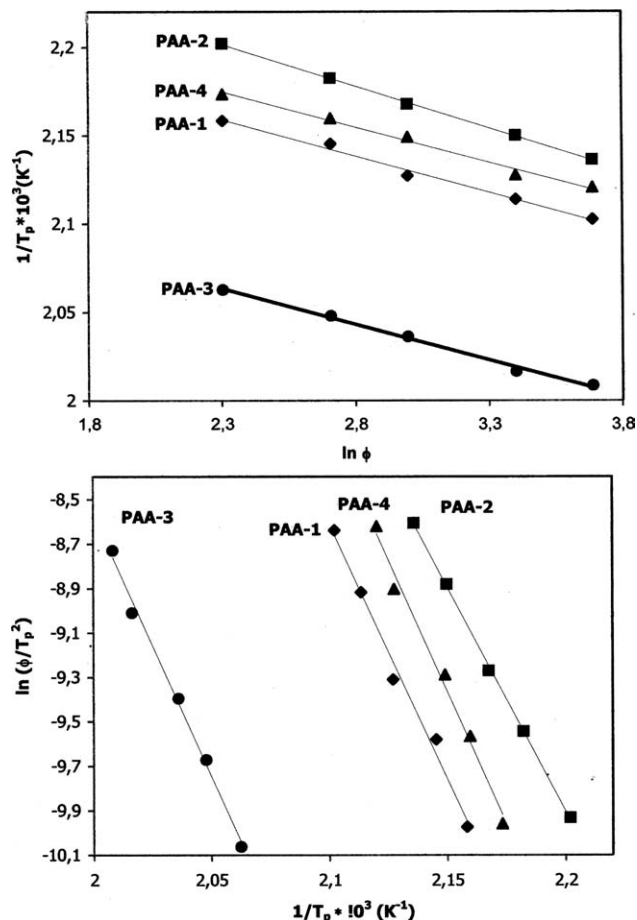


Figure 3 Plots for the determination of E in the imidization reaction by (a) Ozawa method and (b) Kissinger method.

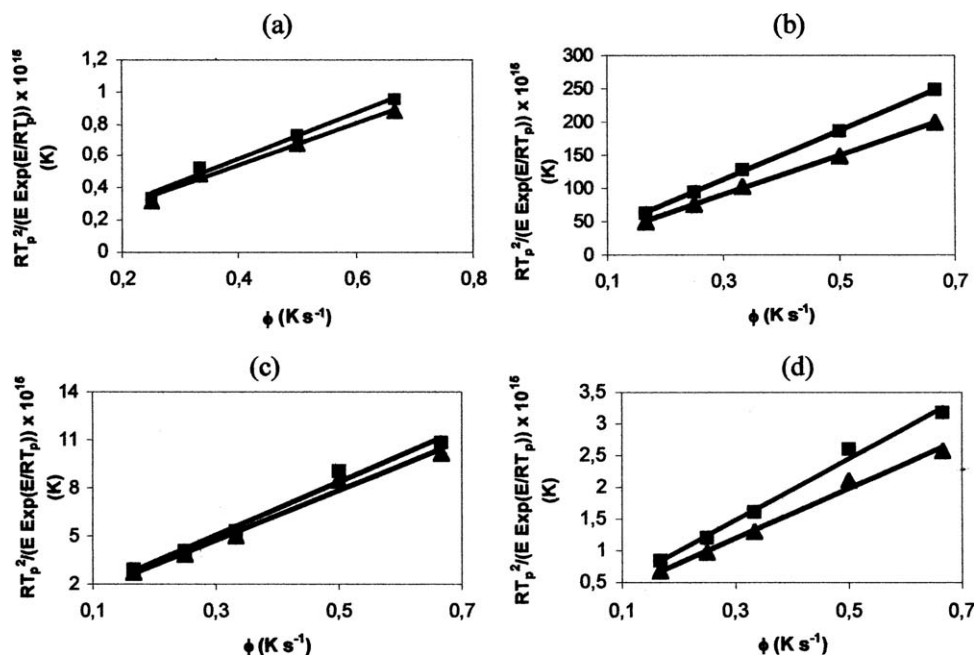


Figure 4 Plots for determination of A from Kissinger equation [eq. (3)], with E estimated from Ozawa method (■) and from Kissinger method (▲), in the imidization reaction of (a) PAA-1, (b) PAA-2, (c) PAA-3, and (d) PAA-4.

of the imidization peak. Considering the influence of polymer structure on ΔH value it was found that polymers with azobenzene groups (PAA-2–PAA-4) exhibited lower imidization enthalpy than poly(ester amic acid) without chromophore (PAA-1).

Imidization reaction of typical poly(amic acid)s obtained from 4,4'-oxydianiline (ODA) and 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) and ODA reacted with pyromellitic dianhydride (PMDA) exhibited an ΔH value of about 125.9 J/g and 120 J/g, respectively,^{36,37} that is, in similar range as obtained for PAA-1.

On the other hand the value of activation energy is very similar for all studied polymers, except PAA-2 in which azobenzene group are introduced between amide linkages. Here also the lowest pre-exponential factor (A) was estimated. It can be concluded that imidization process easier proceeds in PAA-2 in comparison with others investigated PAA-X. The comparison of estimated pre-exponential factor (A) value revealed relationship between position in which azobenzene group is attached to the poly-

mer chain and number of chromophore moieties in their repeating unit. In polymer with two azobenzene derivatives in repeating units collision between carbonyl and carboxamide groups were less effective in producing imide structures than those in poly(ester amic acid) with one chromophore moiety. The resulting apparent activation energies using the two models (Ozawa and Kissinger) were quite close. The small differences were observed in A value, that is, slightly lower A value was calculated by the Ozawa method. For the first time to our knowledge, the imidization kinetic of polymers with side azobenzene groups was studied. Thus, it is impossible to compare our results with published data. Kinetic of transformation into PI of various poly(amic acid)s and H-bonded complexes of tetracarboxylic acid with various diamines were studied by Artem'eva et al. using gas chromatography and thermogravimetric analysis (TGA).^{38–40} Sung et al. investigated kinetics of thermal imidization of poly(amic acid) made from 4,4'-diaminobenzene and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride in solution using

TABLE I
 E and A Values and Enthalpy of Imidization Reaction (ΔH) for the Poly(ester amic acid) PAA from DSC

Polymer	ΔH (J/g)	Ozawa method		Kissinger method	
		E (kJ/mol)	A (1/s)	E (kJ/mol)	A (1/s)
PAA-1	+111.15	191.35	7.06×10^{19}	191.64	7.58×10^{19}
PAA-2	+85.67	167.08	2.70×10^{17}	167.92	3.36×10^{17}
PAA-3	+56.23	195.61	2.06×10^{19}	196.48	2.54×10^{19}
PAA-4	+57.33	198.07	5.94×10^{20}	198.32	6.34×10^{20}

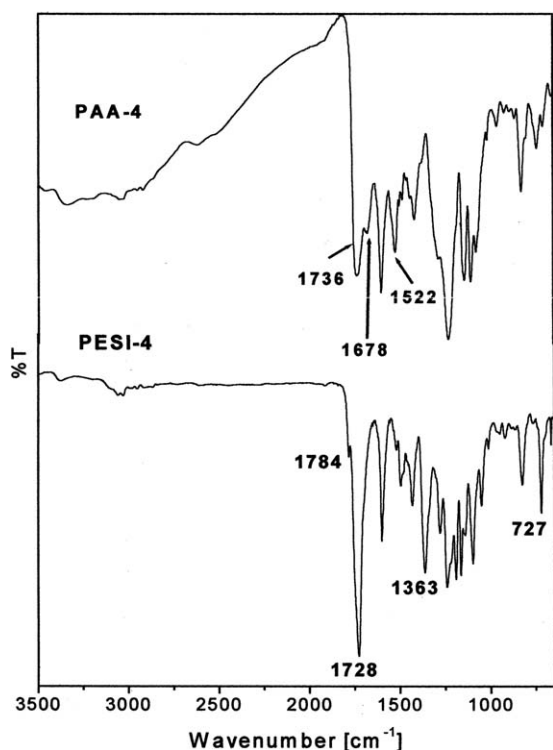


Figure 5 FTIR spectra of poly(ester amic acid) PAA-4 and poly(ester imide) PESI-4.

UV-Vis and IR spectroscopies.⁴¹ Data published for poly(ester amic acid) without azobenzene moieties, that is, obtained from 1,3-phenyldiamine and diesterdianhydride prepared from Bisphenol A was 101,7 kJ/mol and the pre-exponential factor was 1.09×10^{12} , as reported by Seo from FT-Raman spectroscopy.³⁴ Higher activation energy, that is, 130 kJ/mol of poly(amic acid) base on ODA and PMDA imidization from DSC obtained Anthamatten et al.³⁷ and Cano et al.³⁶ for imidization of PAA prepared from BTDA and ODA 148.2 kJ/mol.

Polymer characterization

The formation of poly(ester amic acid)s (PAA-X) and poly(ester imide)s (PESI-X) was confirmed by means of FTIR and ¹H-NMR spectroscopy. All PAA-X were converted to their corresponding poly(ether imide)s by thermal treatment under conditions established from DSC investigations. FTIR spectroscopy allows monitoring of the imide ring formation during thermal curing. A typical set of FTIR spectra for exemplary poly(ester amic acid) PAA-4 and corresponding poly(ester imide) PESI-4 is shown in Figure 5.

FTIR spectra given in Figure 5 showed their distinct peak features of amides and carboxyl groups and imides thus clearly indicating the imide ring formation and disappearance of the amide peak during the cyclodehydration step and the effective conversion of amide to imide. The characteristic absorp-

tion bands of amines and carboxyl groups in the spectra at 3240–3320 and 1500–1730 cm^{-1} region disappeared and those of imide ring appeared near 1784 cm^{-1} a weak absorption and strong absorption at 1728 cm^{-1} , assigned to asymmetric and symmetric stretching vibration of C=O in imide ring, at 1363 (C–N stretching) and 721 cm^{-1} (imide ring deformation). In ¹H-NMR spectra of PAA-X showed the resonance signals of amide protons at 10 ppm and broad signal of carboxylic group protons at range 12 ppm. The protons of methyl groups (–CH₃) are observed around 1,70 ppm. As the imidization proceeded the amide and carboxylic protons peaks completely disappeared. ¹H-NMR and FTIR spectra of the polymers were consistent with their assigned structures.

The best material for many applications should be highly amorphous. Thus, the supramolecular structure of the obtained polymer was evaluated by wide-angle X-ray diffraction experiments.

The X-ray diffraction patterns presented in Figure 6 of the solid poly(ester imide)s and exemplary poly(ester amic acid) PAA-4 showed broad halo patterns without any significant crystalline peaks in the XRD spectral window range from $2\theta = 10^\circ$ to 35° indicating that the polymers were completely amorphous.

Solubility properties

The solubility properties of all polymer, that is, poly(ester amic acid)s (PAA-X) and poly(ester imide)s (PESI-X) were determined qualitatively by the dissolution of 10 mg of the solid polymer in 1 mL of organic solvent and the results are reported in Table II.

All poly(ester amic acid)s containing the azobenzene units (PAA-2–PAA-4) showed an excellent

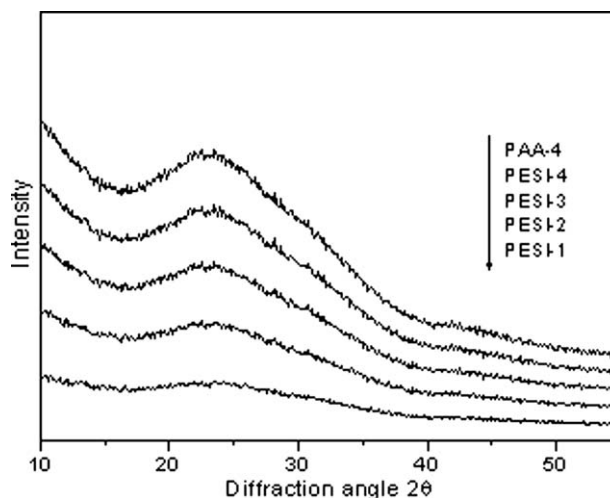


Figure 6 X-ray diffraction patterns of solid PESI-X and PAA-4.

TABLE II
Solubility Behavior of Polymers

Polymer	Solvents ^a						
	DMF	DMSO	<i>m</i> -Cresol	Pyridine	THF	CHCl ₃	CH ₃ CN
PAA-1	+	+	±	+	++	-	-
PAA-2	+	+	++	+	+	-	±
PAA-3	+	+	++	+	+	-	±
PAA-4	+	+	++	+	+	-	±
PESI-1	-	-	-	-	-	-	-
PESI-2	+	+	++	+	+	+	±
PESI-3	±	±	±	±	±	±	±
PESI-4	+	+	+	+	+	+	±

^a The qualitative solubility was tasted with 10-mg samples in 1 mL of solvent. +, soluble at room temperature; ++, soluble on heating; ±, partial soluble on heating; -, insoluble on heating. Solvents: DMF, *N,N*-dimethylformamide; DMSO, dimethylsulfoxide; THF, tetrahydrofuran.

solubility in aprotic polar solvent, such as NMP, DMF, and DMSO and were also soluble in less polar solvent, such as *m*-cresol, pyridine, and THF. PAA-2–PAA-4 were no soluble in chloroform and only partially soluble in acetonitrile. On comparing the solubility behavior of PAA-1–PAA-4 with the analogs poly(ester imide)s (PESI-1–PESI-4) revealed a relatively decreased solubility in PESI-1 and PESI-3. On the other hands the polymers in imidized form (PESI-2–PESI-4) showed better solubility in CHCl₃. Azobenzene-functionalized polymers (PAA-2–PAA-4 and PESI 2–PESI 4) showed better solubility than the corresponding polymer without chromophore, that is, PAA-1 and PESI-1. The increased solubility of chromophore functionalized polymers may be caused by existence of pendant azobenzene groups that led to loose chain packing and to the decrease of the intermolecular interactions.

Thermal properties

Thermal properties of the prepared PESI-X were examined by DSC. The glass transition temperatures (T_g), defined by the midpoint of the base line shift of the polymers, were observed between 217–236°C. All PESI-X gave similar DSC profiles with no melting endotherms and a clear T_g . These findings also clearly indicated their amorphous nature. The glass transition temperature of PESI-X are summarized in Figure 7.

It is obvious that T_g depend on the structure of the polymers. Considering the polymer backbone microstructure it was found that the polymer without azobenzene units possessed the highest T_g . The T_g of polymers decreased after functionalization with azobenzene group. Moreover, the number of azobenzene moieties in polymer repeating unit also affects the T_g values. The lowest T_g exhibited polymer with two chromophores in repeating unit, that is, PESI-4. PESI-X were stable up to 320°C no

decomposition in DSC thermogram was observed for this temperature. All azopolymers display high thermal stability that can be ascribed to imide groups and fulfill thermal requirements for constructing of optical devices.⁴²

Optical properties

The optical properties of polymers were examining by UV–Vis spectroscopy. UV–Vis spectra of polymers were acquiring both in NMP solution and in polymer films on a glass. The range of UV–Vis measurements was limited by transparency of the used solvent and substrate. The representative absorption spectra of polymers PAA-4, PESI-4, and PESI-4 are compared in Figure 8.

Polymers without azobenzene units (PAA-1 and PESI-1) exhibited no absorption in the range above 350 nm [cf. Fig. 8(a)]. Whereas the spectra of polymers with azobenzene units showed a strong absorption band with a maximum at the range of 332–375 nm and a shoulder (at about 450 nm), which are assigned to electronic transitions of *trans*-azochromophores.⁴³ In all cases positions of the azobenzene absorption band of polymers were changed as compared with that of monomer 2,4-diamine-4'-methylazobenzene. Absorption maximum λ_{\max} for 2,4-diamine-4'-methylazobenzene was at 422 nm.¹³

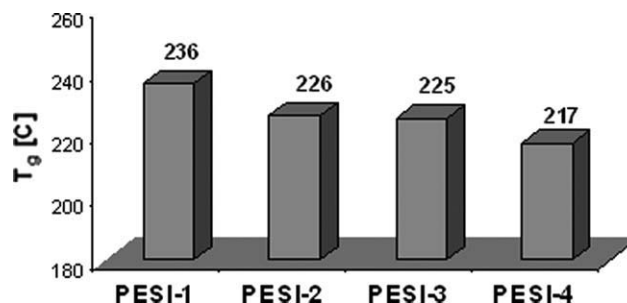


Figure 7 Glass transition temperatures of PESI-X.

Significant blue shift (about 80 nm) of azobenzene λ_{\max} between PAA-2, PAA-4, PESI-2, and PESI-4 and the diamine was ascribed to the reduced electron-donating ability of amino groups upon conversion to the amides and imides; the strongest electron donating substituent is the amino group ($-\text{NH}_2$), followed by the amide group ($-\text{NHCO}-$), and finally the imide group ($-\text{N}(\text{CO}_2)-$).⁴⁴ Electronic spectra of the studied azopolymers show similar characteristics, that is, absorption band in the UV region at 263 nm that is attributed to transition within the polymer backbone, and absorption of the azobenzene derivative. The optical data, absorption (λ_{\max}) maxima of the polymers are collected in Table III.

In most cases positions of the λ_{\max} absorption bands of poly(ester amic acid)s were slightly changed when compared with that of corresponding poly(ester imide)s. Absorption spectra of the polymers in solution and films exhibit the same shape [cf. Fig. 8(b)] and the position of λ_{\max} in the poly-

TABLE III
Absorption Maxima (λ_{\max}) of the Polymers in NMP Solution and in Films Deposited Onto Glass Slides and λ_{\max} of the Chromophores in NMP Solution

Polymer	λ_{\max} (nm)	
	in NMP	in film
PAA-1	273, 308 ^a	-
PAA-2	267, 358, 413 ^a , 448 ^a	368, 453 ^a
PAA-3	269, 311, 332, 444 ^a	-
PAA-4	263, 351, 414 ^a , 449 ^a	351, 449 ^a
PESI-1	284, 310 ^a	-
PESI-2	264, 375, 311 ^a , 459 ^a	351, 447 ^a
PESI-3	264, 364 ^a , 451 ^a	360, 452 ^a
PESI-4	264, 353, 460 ^a	342, 468 ^a

^a The position of absorption band calculated using the second derivatives method (i.e., the minimum of the second derivative of absorption corresponds to the absorption maximum).

mers, when they are casted on glass-solid films, is almost the same in comparison with which they exhibited in solution (cf. Table III).

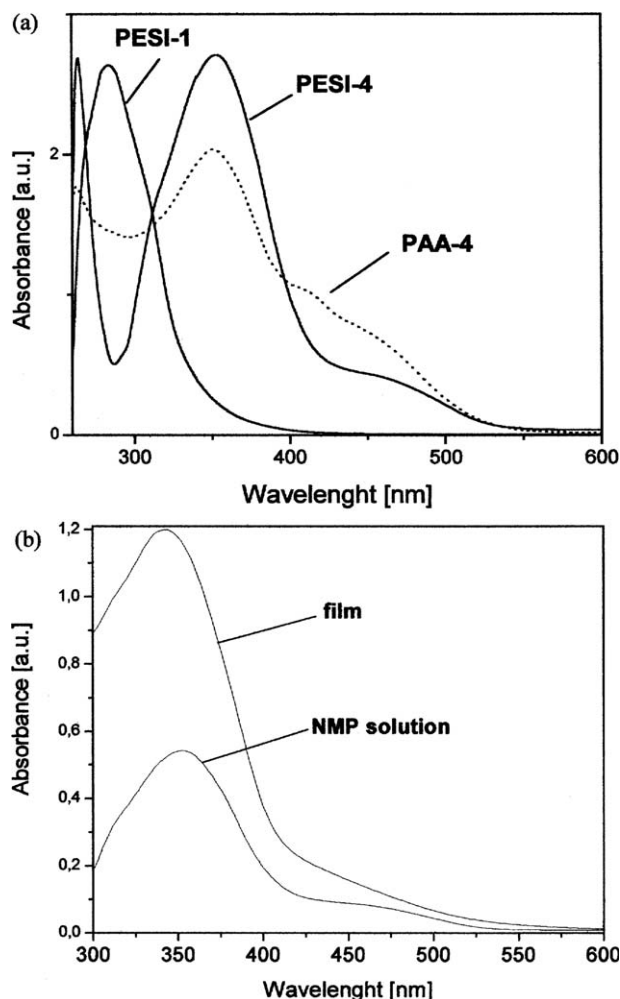


Figure 8 UV-Vis spectra of PAA-4, PESI-4, and PESI-1 in NMP solution (a) and PESI-4 in NMP and in the solid state.

CONCLUSIONS

The objective of this article was to characterize the kinetic parameters of the imidization process of novel poly(ester amic acid)s to poly(ester imide)s occurring in the solid state and the chosen properties of obtained PIs after cyclodehydration. The kinetic parameters (E , A) for investigated PAA-X estimated by using Ozawa and Kissinger methods are almost the same. Comparison of the E and A values from the point of view of polymer backbone microstructure reveals influence position in which azobenzene group is attached to the polymer chain and number of chromophore moieties in their repeating unit. The lowest activation energy was characteristic for polymer prepared from 2,4-diamine-4'-methylazobenzene and diesterdianhydride without azobenzene group (PAA-2). In this case collision between carbonyl and carboxamide groups were more effective in producing imide structures than those in other poly(ester amic acid)s. The obtained poly(ester imide)s exhibited very good solubility and thermal stability and due to presence of azobenzene units and can be considered as material for investigation of light-induced optical anisotropy for potential applications in optical devices and optical elements fabrication. Such study is expected to be useful for the development of 'PI for photonics.'

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