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POLYMERIZATION OF N(p-PHENOXY-PHENYL)ACRYLAMIDE AND COPOLYMERS WITH STYRENE

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ABSTRACT

Copolymerization of N(p-phenoxy-phenyl)acrylamide (PhOPhAA) with styrene (St) in butanone at 70°C under different monomer-to-monomer ratios in the feed using AIBN as free-radical initiator is described. The total monomer concentration was 1 mol L⁻¹. The copolymer composition was evaluated by the nitrogen content in copolymers. The reactivity ratios determined by the Kelen-Tüdös method indicates the random arrangement of monomers in the copolymer chain with an azeotropic point at the equimolar ratio of comonomers. Mean sequence length distribution in copolymers was estimated from r_1 (PhOPhAA) = 0.53 and r_2 (St) = 0.48. Activation energy determined by the Arrhenius method is 118 kJ mol⁻¹. Copolymers are thermally stable up to a temperature of 400°C under TGA conditions. T_g 's and higher transition temperatures increase by increasing the content of PhOPhAA in copolymers. The same was also found for molecular weights of copolymers.

Key Words: N(p-Phenoxy-phenyl)acrylamide; Poly[N(p-phenoxy-phenyl)acrylamide]; Poly[N(p-phenoxy-phenyl)acrylamide-co-styrene]; Mechanism of copolymerization; Reactivity ratios; Mean sequence length; Thermal properties

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INTRODUCTION

In a recently published paper we described the preparation and properties of poly[N-(p-phenoxy-phenyl)methacrylamide] [poly(PhOPhMAA)] and copolymers with various amounts of styrene in copolymer chains [1]. In a continuation of this work, the present paper describes the preparation of N(p-phenoxy-phenyl)acrylamide (PhOPhAA) and copolymerization to low conversion with styrene (St). The aim of this work is to describe the mechanism of homopolymerization, copolymerization, and properties of poly(PhOPhAA) and poly(PhOPhAA-co-St) and to compare these data with those previously described in the polymerization and copolymerization of PhOPhMAA with St.

EXPERIMENTAL

Chemicals

p-Phenoxy-phenylamine, Fluka Chimica-Biochimica, Analitika; Acrylic Anhydride, Polysciences Inc.; Acrylic Acid and Diisopropylcarbodiimide, Aldrich Chemical Company, Inc.

Synthesis of N(p-Phenoxy-phenyl)acrylamide (PhOPhAA)

Method A

A solution of 3.78 g (0.03 mol) of acrylic acid anhydride in 20 mL of Et₂O was slowly added to a solution of 5.55 g (0.03 mol) of phenoxy-phenylamine in 80 mL of Et₂O, and the dark solution was left overnight at room temperature. Half of the solvent was evaporated in vacuum and the crystalline product was filtered off, yielding 4.8 g (67%) of PhOPhAA; m.p. 115-116°C.

Analysis: Calcd. for C₁₅H₁₃NO₂ (239); C, 75.31; H, 5.44; N, 5.86. Found: C, 75.38; H, 5.70; N, 5.79.

Method B

A solution of 5.76 g (5.48 mL, 0.08 mol) of acrylic acid in 4 mL of THF was added under cooling to a solution of 5.05 g (6.25 mL, 0.04 mol) of diisopropylcarbodiimide in 80 mL of THF cooled to 10°C. After standing overnight at room temperature, the crystalline product was removed by filtration, washed with 2 mL of THF, yielding 5.03 g (87%) of white crystals melting at 190-195°C (under the sublimation at 140°C). According to the elemental analysis, the product corresponds to diisopropylurea.

Analysis: Calcd. for $C_7H_{16}N_2O$ (144); C, 58.33; H, 11.16; N, 19.16. Found: C, 58.12; H, 10.73; N, 19.16.

Mother liquor was evaporated in vacuum, yielding 5.34 g of an oily product which was dissolved in 20 mL of Et_2O , and slowly added to a solution of 6.4 g of $PhOPhNH_2$ in 80 mL of Et_2O . Half the volume of the dark solution was evaporated and the residue was left overnight in a refrigerator. The crystalline product was filtered off yielding 5.0 g (60%, based on $PhOPhNH_2$) of $PhOPhAA$; m.p. 114-115°C. The product for polymerization was recrystallized from THF-petroleum ether; yield 4.5 g, m.p. 115-116°C.

Analysis: Calcd. for $C_{15}H_{13}NO_2$ (239); C, 75.31; H, 5.44; N, 5.86. Found: C, 75.16; H, 5.66; N, 5.80.

Polymerization Procedure

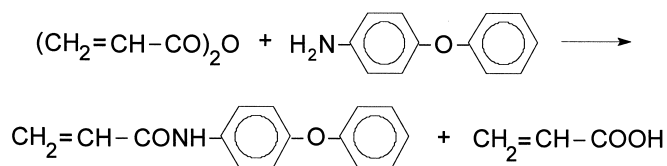
Polymerization was performed in vacuum-sealed glass vials filled with nitrogen, and placed into an oil bath thermostated at 65°C, 70°C, and 75°C, respectively. The polymerization was performed with 1 wt% of AIBN to conversions not exceeding 20% at different monomer-to-monomer ratios in the feed in butanone at a total comonomer concentration of 1 mol L^{-1} . The viscous solution of polymers was diluted with $CHCl_3$ and precipitated with a large excess of *i*-PrOH at 30°C.

Physicochemical Measurements

NMR spectra were performed on a Varian EM 390 Spectrometer. The copolymer composition was determined by elemental analysis. Molecular weights were determined on a Varian HPGPC Model 5800 using a set of 4 mStyrogel columns with THF as solvent and polystyrene standards. A Perkin-Elmer model DSC-2 was used for T_g determination in nitrogen with a sample size of 15 mg and a scanning rate of 40°C min^{-1} . The thermogravimetric analysis was carried out on a Perkin-Elmer TGS-2 thermogravimetric system in a nitrogen stream with a heating rate of 10°C min^{-1} .

RESULTS AND DISCUSSION

N(*p*-Phenoxy-phenyl)acrylamide ($PhOPhAA$) was prepared by the condensation of acrylic acid anhydride with $PhOPhNH_2$, following the reaction presented in Scheme 1. $PhOPhAA$ is a relatively stable monomer which can also be obtained by condensation of $PhOPhNH_2$ with crude acrylic acid anhydride prepared by the condensation of acrylic acid with diisopropylcarbodiimide. In both cases, the $PhOPhAA$ can be separated without the addition of an inhibitor. The aim of this paper is to describe the mechanism of homopolymerization, copolymerization and



Scheme 1. Synthesis of N(p-phenoxy-phenyl)acrylamide.

properties of poly(PhOPhAA) and poly(PhOPhAA-co-St) prepared by free-radical initiated polymerization to low conversion, and to compare these data with those previously described in the polymerization and copolymerization of PhOPhMAA with St [1].

As shown in Figure 1, the copolymerization of PhOPhAA with St is a statistical reaction with azeotropic composition at an equimolar ratio of comonomers in the feed and in copolymer. It is also evident that copolymers prepared under different ratios of comonomers in the feed have a high tendency to form ideal copolymers. The experimental data of copolymerization of PhOPhAA with St at different temperatures are summarized in Table 1. The copolymerization composition is determined from the nitrogen content.

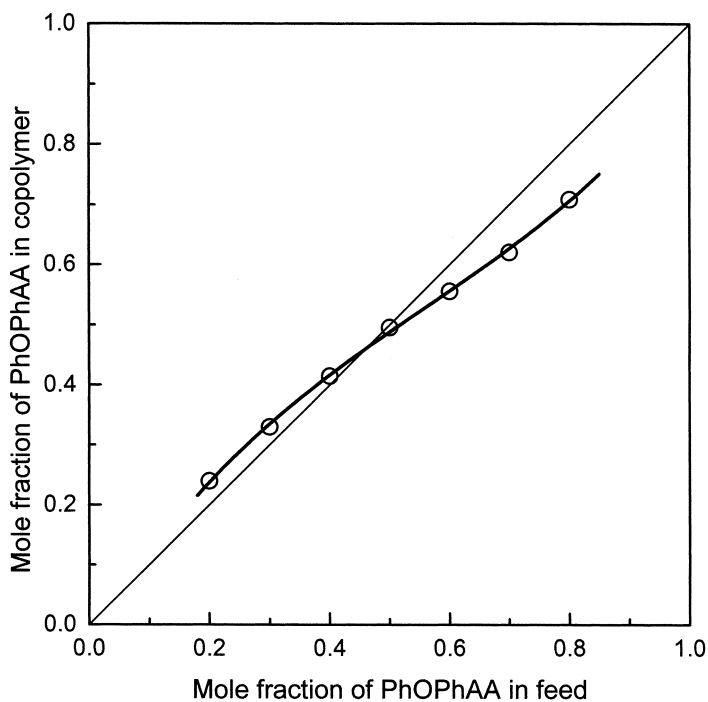


Figure 1. Ratio of molar fraction of PhOPhAA in feed and in copolymers with St; copolymerization is performed in butanone at 70°C with 1 wt% of AIBN.

Table 1. Polymerization Conditions and Properties of Poly(PhOPhAA-co-ST) in 2 mL of Butanone at a Total Comonomer Concentration of 1 mol L⁻¹ at 70°C with 1.0 wt% of AIBN

PhOPhAA (M ₁)	Molar Fraction of		Polym. Time (min)	Polymer Yield (g)	Convers. (%)	N (%)	T _g (°C)	T _{trans.} (°C)	Molecular Weight (g mol ⁻¹)
	St (M ₂)	PhOPhAA (M ₁) ^a							
	in copolymer								
0.2	0.8	0.240	0.760	0.0362	13.82	2.46	113	310	
0.3	0.7	0.330	0.670	0.0429	14.84	3.11	121	340	13.0
0.4	0.6	0.415	0.585	0.05535	17.52	3.63	126	352	
0.5	0.5	0.496	0.504	0.0685	19.97	4.06	132	357	17.3
0.6	0.4	0.556	0.444	0.0791	21.38	4.35	137	360	
0.7	0.3	0.621	0.379	0.06475	16.33	4.63	138	367	54.9 ^b
0.8	0.2	0.709	0.291	0.0659	15.54	4.97	142	370	
1. ^a	0.	1.	0.	0.0852	35.65	5.88	155	373	

^aIn the presence of 0.4 wt.% of AIBN.

^bM_w at 70°C with 0.4 wt.% AIBN is 91200 g mol⁻¹.

In order to characterize the copolymer sequences, the monomer reactivity ratios r_1 and r_2 were determined following the Kelen-Tüdös treatment according to Equation 1:

$$\eta = \left(r_1 + \frac{r_2}{\alpha} \right) \frac{\xi}{\alpha} \quad (1)$$

where η and ξ are mathematical functions of molar composition ratios of monomers in feed and in copolymers, and α is an arbitrary parameter [2].

Reactivity ratios determined from Figure 2, using the least square fit method are r_1 (PhOPhAA) = 0.53 and r_2 (St) = 0.48; $a = 1.1404$.

The mean sequence length could be determined using Equations 2 and 3 [3, 4]:

$$\bar{l}_1 = r_1 \frac{[M_1]}{[M_2]} + 1 \quad (2)$$

$$\bar{l}_2 = r_2 \frac{[M_2]}{[M_1]} + 1 \quad (3)$$

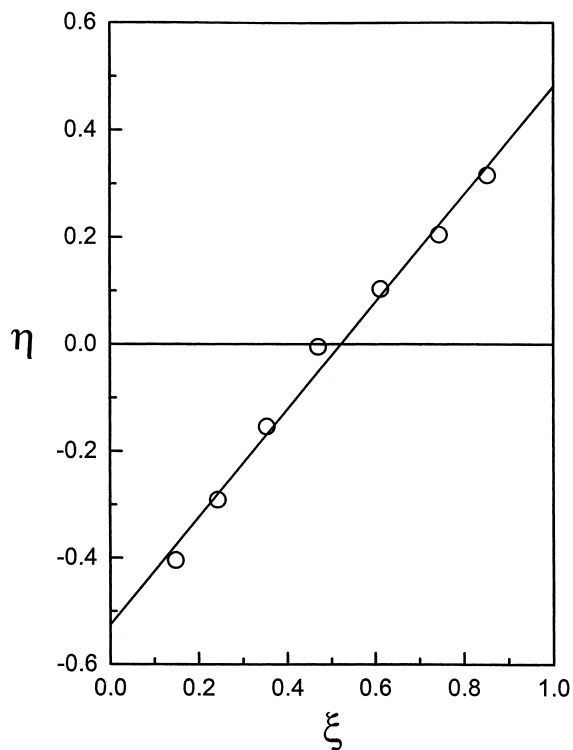


Figure 2. Kelen-Tüdös diagram for calculation of r_1 (PhOPhAA) = 0.53 and r_2 (St) = 0.48; $\alpha = 1.1404$.

The mean sequence lengths are given in Table 2. The data in Table 2 indicate that at equimolar ratio of comonomers in the feed, the copolymers are alternating, while at 80% of St (M_2) in the feed, the mean sequence distribution corresponds to one PhOPhAA to three St and at 80% of PhOPhAA (M_1) in the feed the copolymer consists of blocks of $M_1 M_1 M_1 M_2$.

Time-conversion curves in the copolymerization of PhOPhAA with St at 65°C, 70°C, and 75°C, respectively, at equimolar ratio of comonomers in the feed are shown in Figure 3.

The linear relationship in the plot of $[M_0]/[M_t]$ vs. time, indicates that the copolymerization of PhOPhAA with St is a first order reaction in PhOPhAA as shown in Figure 4.

Rate constants of the copolymerization at 65°C, 70°C, and 75°C, respectively, are determined as slopes of straight lines in Figure 4: $k_{65} = 0.0005 \text{ min}^{-1}$; $k_{70} = 0.001042 \text{ min}^{-1}$; $k_{75} = 0.001817 \text{ min}^{-1}$. The activation energy was calculated by the Arrhenius method using the equation:

$$E_A = \text{tg } \alpha \cdot R / 0.4343 \quad (4)$$

where E_A is the activation energy, $\text{tg } \alpha$ is the slope of the straight line from the plot of the decimal logarithm of the rate constants vs. the reciprocal absolute temperature, and R is the gas constant (Figure 5).

The energy of activation in the copolymerization of PhOPhAA with St in butanone with AIBN as initiator is 118 kJ mol^{-1} . It is of interest to note that the activation energy in the copolymerization of PhOPhMAA with St has a value of $71.24 \text{ kJ mol}^{-1}$ [1].

Figure 6 shows the initial rates of copolymerization PhOPhAA with St in copolymers vs. molar fraction of PhOPhAA with St in feed in the presence of 1 wt% of AIBN in butanone at 70°C. The same figure shows the rate of copolymerization of PhOPhMAA with St in toluene at 70°C and 0.5 wt% of AIBN [1].

Table 2. Mean Sequence Lengths in Copolymerization of PhOPhAA (M_1) with St (M_2) in Butanone at 70°C with 1 wt% of AIBN

Molar Fraction of PhOPhAA in Feed	$\bar{l}_1 = r_1 \frac{[M_1]}{[M_2]} + 1$	$\bar{l}_2 = r_2 \frac{[M_2]}{[M_1]} + 1$	$\bar{l}_1 : \bar{l}_2$	Distribution
0.2	1.13	2.92	1 : 3	$M_1 M_2 M_2 M_2$
0.3	1.23	2.12	1 : 2	$M_1 M_2 M_2$
0.4	1.35	1.72	1 : 2	$M_1 M_2 M_2$
0.5	1.53	1.48	1 : 1	$M_1 M_2$
0.6	1.80	1.32	2 : 1	$M_1 M_1 M_2$
0.7	2.24	1.20	2 : 1	$M_1 M_1 M_2$
0.8	3.12	1.12	3 : 1	$M_1 M_1 M_1 M_2$

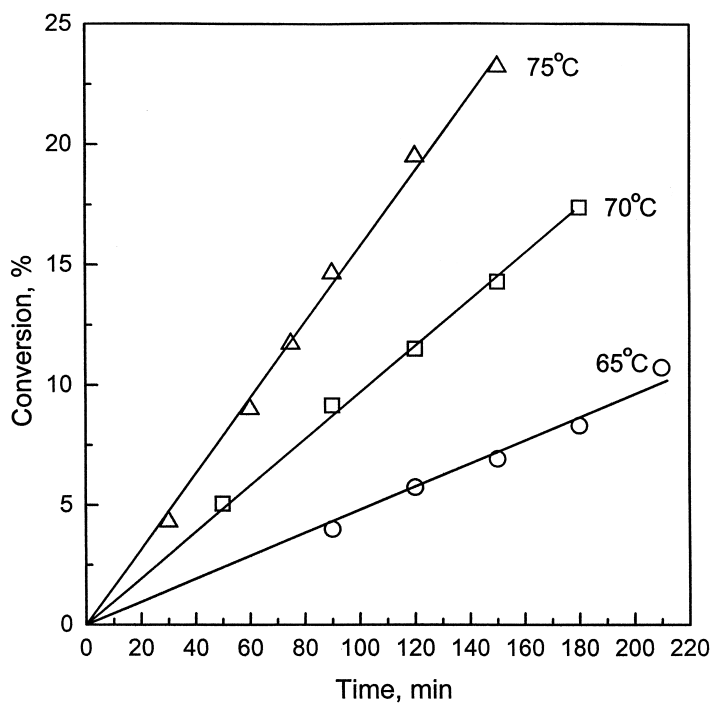


Figure 3. Time-conversion curves in the copolymerization of PhOPhAA with St at 65°C, 70°C, and 75°C in butanone; 1 wt% AIBN.

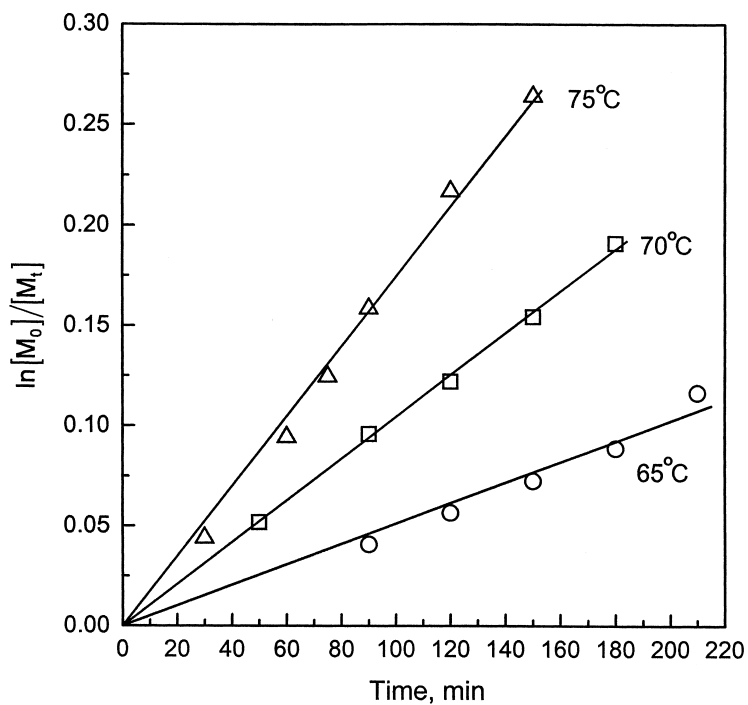


Figure 4. First-order rate plots of the copolymerization of PhOPhAA with St at 65°C, 70°C and 75°C in butanone; 1 wt.% AIBN.

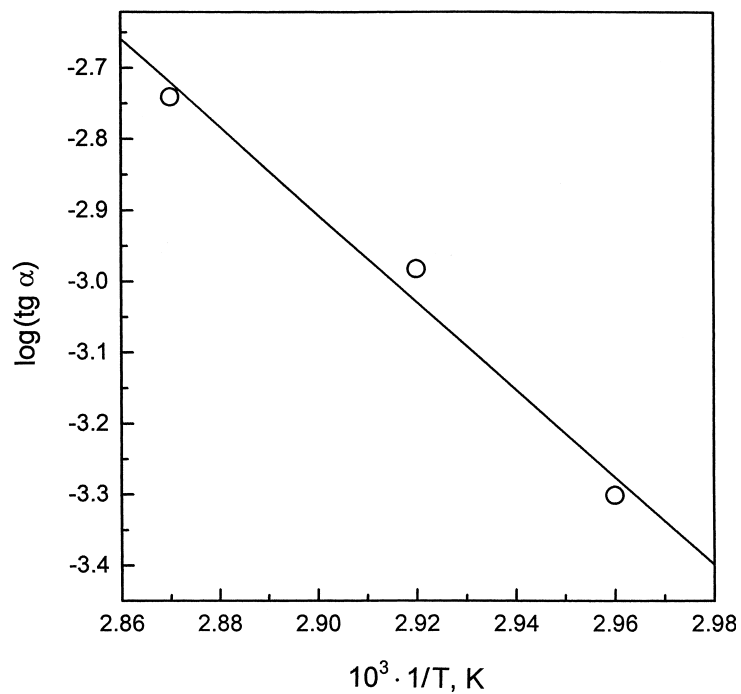


Figure 5. The relationship between logarithm of rate constants vs. reciprocal values of absolute temperature in the copolymerization of PhOPhAA with St in butanone; 1 wt% of AIBN

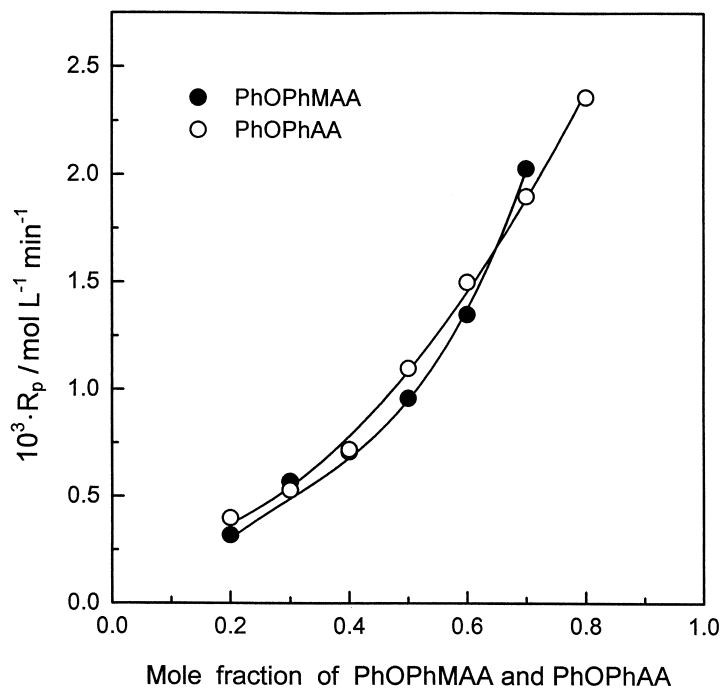


Figure 6. Rates of copolymerization of PhOPhMAA with St (●) [1] and PhOPhAA with St (○) vs. mole fraction in feed.

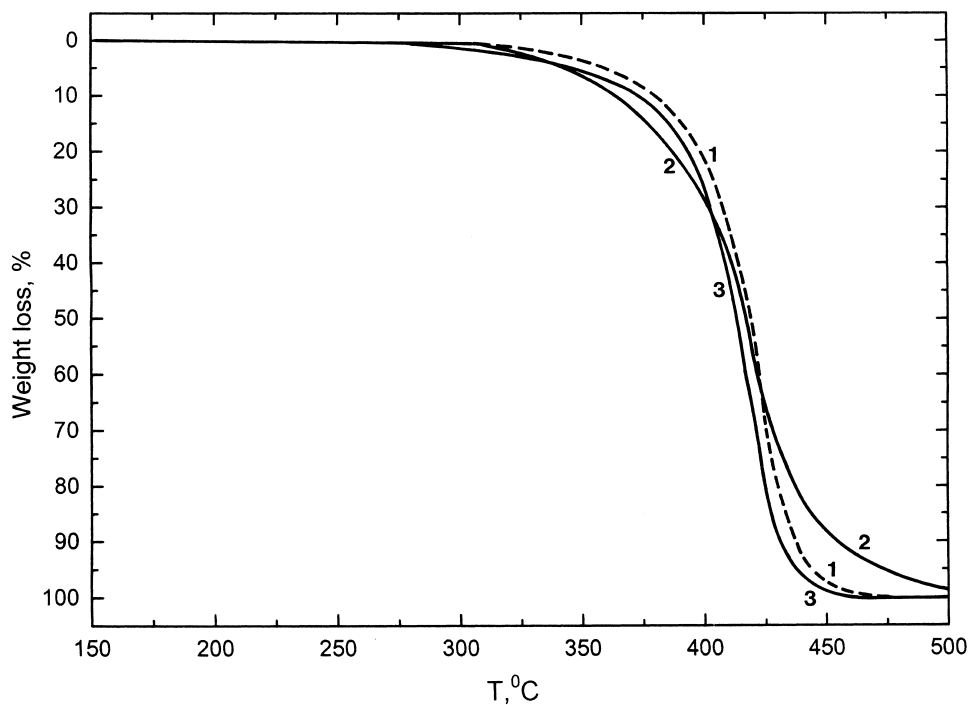


Figure 7. Comparison of thermograms of copolymer poly(PhOPhAA-co-St); molar ratio of comonomers 0.5:0.5 (1), and homopolymers: poly(PhOPhAA) (2) and poly(St) (3).

Thermograms of copolymer prepared under molar ratio of 0.5 : 0.5 in the feed, and thermograms of poly(PhOPhAA) and poly(St) are presented in Figure 7. The thermograms indicate that the thermal stability of copolymer is similar to the stability of poly(St) prepared under the same conditions. All tested polymers decompose by a one-step mechanism to complete loss of weight. Decomposition temperatures: T_{initial} (T_i), T_{maximal} (T_{max}) and T_{final} (T_f) of poly(PhOPhAA-co-St), poly(PhOPhAA) and poly(St) Calcd. according to the procedure proposed by Jia and coworkers [5] are presented in Table 3.

Table 3. TGA Results for Poly(PhOPhAA-co-St), Poly(PhOPhAA) and Poly(St)

Molar Fraction of PhOPhAA in Feed	T_i (°C)	T_{max} (°C)	T_f (°C)
0.2	360	382	440
0.5	370	410	440
0.7	347	440	435
1.	368	392	445
poly(St)	355	400	435

TGA thermogram of poly(St) almost fully coincides with the TGA values of poly(PhOPhAA-co-St) prepared at equimolar ratio of comonomers in the feed.

T_g 's and T_{trans} of poly(PhOPhAA-co-St) at different monomer ratios of comonomers in the feed are presented in Table 1. It is evident that T_g values increase linearly with the increase of PhOPhAA in copolymers and that T_{trans} are in all studied copolymers within the thermally stable region, thus indicating the possible existence of regular domains in the mesophase. Similar results are obtained in the copolymers of PhOPhMAA with St [1].

As expected from the values of mean sequence distribution in copolymerization of PhOPhAA with St presented in Table 2, the molecular weights of copolymer which contain a higher amount of PhOPhAA in copolymer are higher than those containing a higher amount of St (Table 1).

CONCLUSION

N(p-Phenoxy-phenyl)acrylamide (PhOPhAA) was prepared by condensation of acrylic acid anhydride with p-phenoxy-phenylamine in Et₂O at room temperature.

Homopolymerization of PhOPhAA and copolymerization with St was performed in butanone in the presence of 1 wt% of AIBN at 70°C. The copolymerization was a statistical reaction with an azeotropic composition of PhOPhAA to St at a molar ratio of 0.5 to 0.5. Reactivity ratios determined by Kelen-Tüdös method are r_1 (PhOPhAA) = 0.53 and r_2 (St) = 0.48. The mean sequence length distribution shows that at equimolar ratio of comonomers in the feed, the copolymers are alternating, while at an excess of St in the feed, the copolymer blocks contain 3 St to 1 PhOPhAA, and at 80% of PhOPhAA in the feed, copolymer blocks have opposite distribution of comonomers.

Molecular weights of copolymers which contain a higher amount of PhOPhAA in copolymer are higher than those containing a higher amount of St.

Energy of activation, $E_A = 118 \text{ kJ mol}^{-1}$, is determined by the Arrhenius method on the basis of initial rates of copolymerization at 65°C, 70°C, and 75°C, respectively. It is of interest to note that thermograms determined by TGA of all copolymers, poly(PhOPhAA) and poly(St) are similar and stable up to 400°C with initial decomposition temperatures at about 350°C to 370°C. Glass transition and higher transition temperatures of copolymers increase when PhOPhAA is increased in the polymer chains. T_g 's and T_{trans} are within the thermally stable region, thus indicating the possibility of existence of regular domains in polymer chains.

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