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Free-Radical-Initiated Polymerization of N(p-Phenoxy-phenyl)maleimide and Copolymerization with Styrene, α-Methylstyrene and β-Methylstyrene

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FREE-RADICAL-INITIATED POLYMERIZATION OF N(p-PHENOXY-PHENYL)MALEIMIDE AND COPOLYMERIZATION WITH STYRENE, α-METHYLSTYRENE AND β–METHYLSTYRENE

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ABSTRACT

Synthesis and free-radical-initiated homopolymerization of phe-noxy-phenylmaleimide (PhOPhMI) and copolymerization with sty-rene (St), (α-methylstyrene (αMeSt) and β–methylstyrene (β-MeSt) are described. It was found that alternating copolymers are formed under different monomer-to-monomer ratios in the feed and that the mechanism based on the participation of CT-complex best explains the formation of alternating copolymers. Equilibrium constants of CT-complexes are: $K_{PhOPhMI/St} = 0.20 \ Lmol^{-1}$; $K_{PhOPhMI/\alpha MeSt} = 0.05 \ Lmol^{-1}$; $K_{PhOPhMI/\beta MeSt} = 0.02 \ Lmol^{-1}$. Homopolymer and co-polymers are film-forming materials, stable up to 350°C under TGA conditions. T_g s and higher transition temperatures are within the thermally stable region.

INTRODUCTION

Copolymerization of N-arylmaleimides with electron donor monomers has been described in numerous papers, and it was shown that under free-radical-initiated polymerization alternating copolymers are formed [1-3]. The interest in studies of these polymers stems from the fact that they are thermally stable and, due to their comb-like structure, they often show a tendency to smectic ordering in

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H_2N —⬡— O —⬡ + O = C - CH - CH = CH - CO - O ⟶

HOOC - CH = CH - CONH —⬡— O —⬡— COOH $\dfrac{(CH_3CO)_2O}{NaOAc}$ →

O = C - CH = CH - CON —⬡— O —⬡
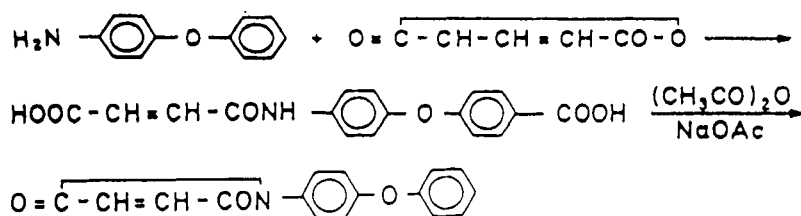
Scheme I. Synthesis of N(p-Phenoxyphenyl)maleimide

amorphous matrix [4,5]. In addition, the N-arylnialeimides are strong electron acceptors and form charge-transfer complexes with many electron donor monomers, thus being suitable models for studies of the mechanism of alternating copolymerization under the participation of CT-complex monomers [6,7]. In continuation of our studies on the preparation of thermally stable alternating copolymers, we shall describe preparation and properties of poly [N(p-phenoxyphenyl)maleimide] and copolymers with styrene, (α—methylstyrene and ß-methylstyrene. Polymerization reactions are performed up to high conversion at equimolar ratios of comonomers and at low conversion at different monomer-to-monomer ratios in feed.

EXPERIMENTAL

Materials

Preparation of N(p-phenoxy-phenyl)maleimide is presented in Scheme 1.

N(p-Phenoxyphenyl)maleamic Acid

A solution of 25.5 g (0.14 mol) of p-phenoxyphenylamine in 50 mL of chloroform was added slowly under cooling into a solution of 13.5 g (0. 14 mol) of maleic anhydride in 100 mL of chloroform and left overnight at room temperature. The yellow crystalline product was filtered off and recrystallized from 300 mL of ethanol yielding 37 g (97%) of long yellow needles soluble in isopropanol, insoluble in benzene; m.p. 172-173ºC.

Analysis: Calculated for $C_{16} H_{13} NO_4$ (%): C, 67.83; H, 4.64; N, 4.95. Found: C, 67.43; H, 4.5 9; N, 4.9 7.

N(p-Phenoxyphenvl)maleimide (PhOPhMI)

N(p-Phenoxyphenyl)maleamic acid (31.62 g, 0.11 mol) was heated under stirring for 45 minutes at 100ºC with 18 mL of acetic anhydride and 4 g of

anhydrous sodium acetate. The dark solution was cooled to room temperature and stirred for one hour with 200 mL of iced water. The dark crystalline product was filtered off, washed with water and dried in vacuum. The crude product (30.6 g) was recrystallized from 100 mL of benzene yielding 20.13 g (69%) of long yellow needles. For analysis, the monomer was recrystallized from isopropanol; mp. 166.5-167.5°C under sublimation at 160°C.

Analysis: Calculated for $C_{16} H_{11} NO_3$ (%): C, 72.44; H, 4.18; N, 5.28. Found: C, 72.38; H, 4.46; N, 5.31.

Polymerization Procedure

Polymerization was performed in vacuum-sealed 10 mL glass vials thoroughly degassed, filled with nitrogen before sealing, and placed into an oil bath thermostated at 70°C. The polymerization initiated with 0.5 wt % of AIBN was performed to high conversion at equimolar ratios of comonomers in toluene or to low conversion at different monomer-to-monomer ratios in the feed in dioxane. The viscous solution of polymers was diluted with chloroform and precipitated by dropwise addition to methanol. The precipitated polymer was filtered off and dried in vacuum overnight at 80°C .

Physicochemical Measurements

NMR spectra were obtained on a Varian EM 390 spectrometer. The copolymer composition was determined by NMR spectroscopy in deuterated dimethylsulfoxide as solvent and by elemental analysis. The equilibrium constants of charge-transfer complexation were determined by the NMR continuous variation method in deuterated chloroform at 35°C, with TMS as the internal reference. Differential scanning calorimetry (DSC) was carried out on a Perkin-Elmer model DSC-2 with a scanning rate of 20°C/min in nitrogen with a sample size of 15 mg. Glass transition temperature, T_g, was taken as the temperature at which the midpoint of the heat capacity change at transition was achieved. 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.

RESULTS AND DISCUSSION

Several approaches have been described in the literature to treat the kinetic data of systems with the anticipated participation of charge-transfer complexes in copolymerization reactions. As shown in previous papers from our Laboratories [1] the treatment of Shirota and coworkers [5,6] makes it possible to separate the

TABLE 1. Polymerization Conditions and Properties of Poly-PhOPhMI (I) and Alternating Copolymers with St, αMeSt and βMeSt;0.5 wt% AIBN in Toluene at 70°C

| Polymer	Conversion % in 24 hrs	Mol.% PhOPhMI in Copolymers by NMR	$M_w \cdot 10^{-3}$ (g/mol)	$M_n \cdot 10^{-3}$ (g/mol)	T_g (°C)	T_{trans} (°C)	Wt. loss (%)			Analysis (%)	
							300°C	350°C	400°C	Calc'd	Found
I	96.0		31.0	18.0	321	367	0.3	1.0	2.0	C, 72.45 H, 4.15 N, 5.28	C, 72.73 H, 4.88 N, 5.17
I-alt-St	92.9	52.6	290.0	85.3	190	304	0.7	1.0	5.4	C, 78.05 H, 5.15 N, 3.79	C, 78.67 H, 5.66 N, 3.82
I-alt-αMeSt	87.8	50.7	77.0	35.7	201	303	0.6	5.2	6.34	C, 78.33 H, 5.48 N, 3.65	C, 78.16 H, 5.84 N, 3.53
I-alt-βMeSt	79.9	50.6	45.1	25.1	220	336	0.2	0.6	8.3	C, 78.33 H, 5.48 N, 3.65	C, 78.46 H, 5.68 N, 3.75
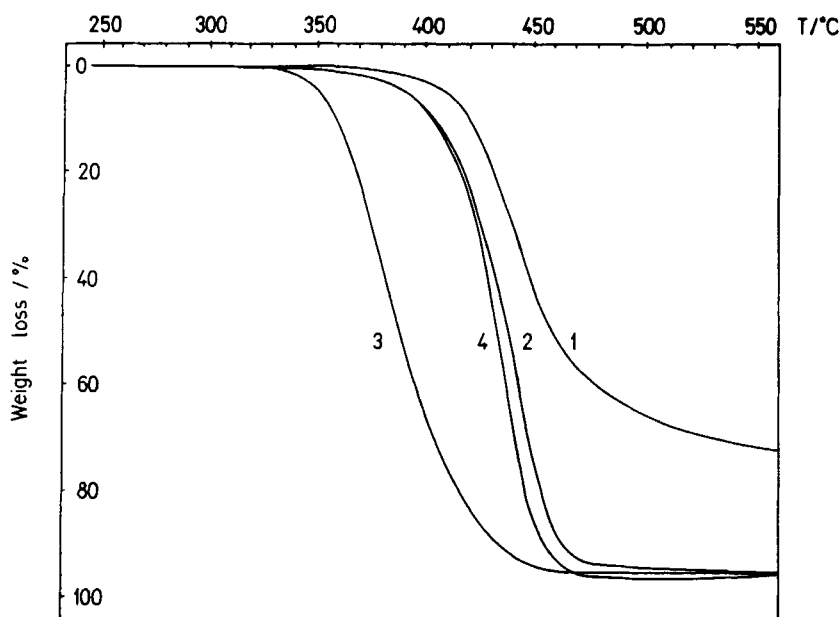
Figure 1. Thermogravimetric analysis of 1) PhOPhMI; 2) poly(PhOPhMI-alt-St); 3) poly(PhOPhMI-alt-αMeSt); 4) poly(PhOPhMI-alt-ßMeSt).

copolymerization reaction via cross-propagation of free monomers and by the addition of CT-complex monomers.

High Conversion Polymerization and Copolymerization

Polymerization and copolymerization conditions and properties of poly-PhOPhMI and copolymers with St, αMeSt and βMeSt are presented in Table 1.

Data in Table 1 indicate that both homopolymer and alternating copolymers, specially copolymers with St, have relatively high molecular weights. It is further evident that all prepared polymers are thermally stable and under the conditions of thermogravimetric analysis the copolymers decompose by one-step mechanism to completion while homopolymer also decomposes by one-step mechanism between 400-500°C, but under the formation of 40% of carbonized residue (Figure 1). It is of interest to note that unsubstituted poly(N-phenylmaleimide) decomposes in a narrow temperature range without the residue while disubstituted poly[4'-N(benzo-15-crown-5)maleimide] similarly decomposes, but 30% of stable carbonized residue is formed at 450°C [4].
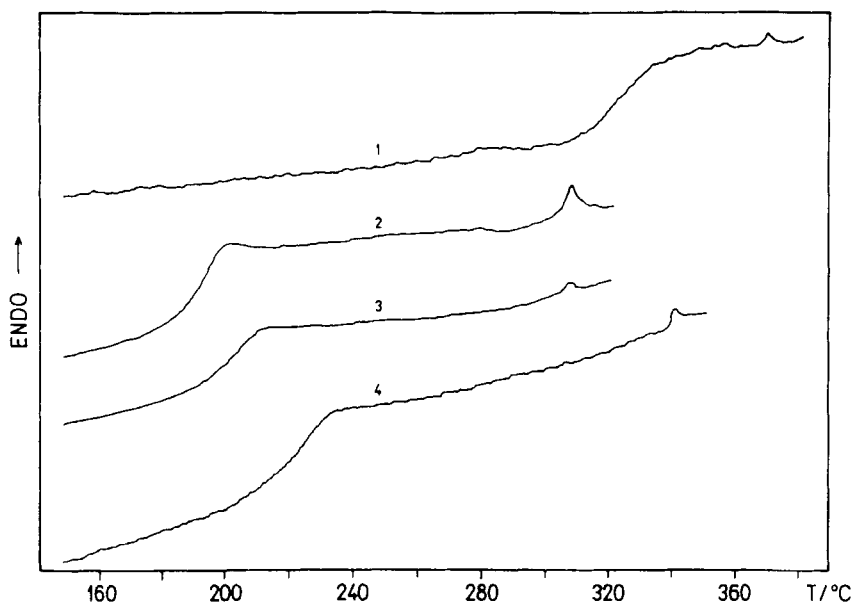
Figure 2. DSC tracings of 1) poly-PhOPhMI; 2) poly(PhOPhMI-alt-St); 3) poly(PhOPhMI-alt-αMeSt); 4) poly(PhOPhMI-alt-ßMeSt); scanning rate 20ºC min-¹ in N_2; second scan.

The same was also found in thermal decomposition of o-, m-, and p-poly-[(ethoxycarbonylphenol)maleimide] [8]. Numerical values and DSC tracings of transition temperature of poly-PhOPhMI and alternating copolymers are presented in Table 1 and Figure 2. It is evident that T_g s and higher transition temperatures in the mezophase of homopolymer are much higher than transition temperatures of copolymers. However, all transition temperatures are within the thermally stable region.

Low Conversion Polymerization at Different Monomer-to-Monomer Ratios in Feed

Similar to the previously studied mechanism of copolymerization of N-substituted maleimides with (α and β-methylstyrene at differentt monomer-to-monomer ratio in feed [1,9], it was found that there is a strong tendency to alternation in the copolymerization of PhOPhMI with St, (αMeSt and βMeSt, and that copolymerization proceeds under the participation of charge-transfer complex monomers.

The formation of CT-complex in copolymerization of PhOPhMI with St, (αMeSt and βMeSt is proved by the change of chemical shifts in PhOPhMI proton
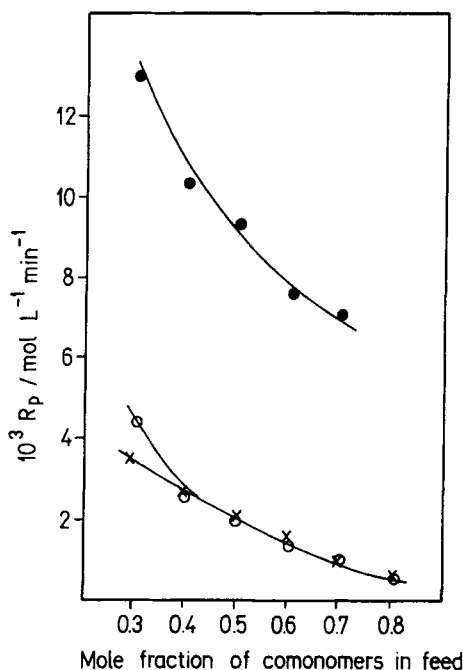
Figure 3. Rate of copolymerization os PhOPhMI with comonomers: (•) St; (o) αMeSt; (x)ßMeSt, 0.5 wt% of AIBN in dioxane at 70°C; total monomer concentration 2 mol L^{-1}.

in the presence of various concentrations of electron donors. The equilibrium constants for monomer complexation were determined by a transformed Benesi-Hildebrand method [10] and the following values of equilibrium constants were obtained: K_{St} = 0.20 Lmol^{-1} ; $K_{\alpha MeSt}$ = 0.05 Lmol^{-1}; $K_{\beta MeSt}$ = 0.02 Lmol^{-1}.

The rate of copolymerization at different monomer-to-monomer concentra-tration in the feed is presented in Figure 3.

It is evident that rate of propagation in the copolymerization with St is much faster than the copolymerization with (αMeSt and βMeSt. In all experiments, conversion was lower than 15% and based on elemental analysis or from NMR data it was proved that alternating copolymers are obtained regardless to the composition of feed. Composition of copolymers measured by NMR is presented in Figure 4.

Assuming that the initial rate of copolymerization Rp equals the sum of the rate of copolymerization of free monomers Rp(f), and the rate of copolymerization of charge transfer complex Rp(CT), Shirota and coworkers [6,7] showed that the plot of Rp/[Mo] against [M$_1$] gives a straight line for each given ratio of monomer
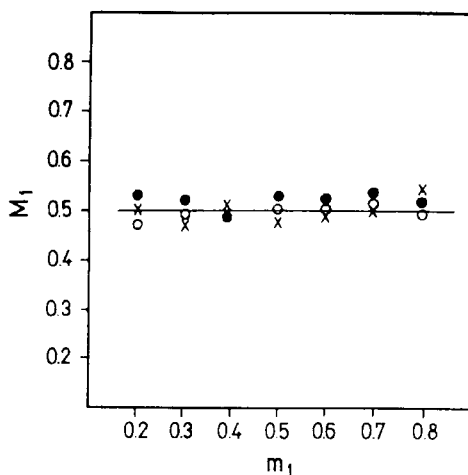
Figure 4. Plot of molar fraction of PhOPhMI in comonomer mixtures (m$_1$), and in copolymers (M$_1$); (•) St; (o) (αMeSt; (x) ßMeSt; (m$_1$) mol. of St, (αMeSt and ßMeSt in feed and in copolymers; in dioxane; 0.5 wt% AIBN at 70°C.

TABLE 2. Relative Participation of Rp(f) and RP(CT) in Copolymerization of PhOPhMI with St, (αMeSt and ßMeSt as Percent of Rp

Copolymer	Momomer Concentration (mol L^{-1})	Rp(f)/% (mol L^{-1} min^{-1})	Rp(CT)/%
polv(PhOPhMI-alt-St)	1	84	16
	2	73	27
poly(PhOPhMI-alt-αMeSt	1	42.3	57.7
	2	29.6	70.4
poly(PhOPhMI-alt-ßMeSt)	1	38.8	61.2
	2	24.3	75.6

concentration X= [M$_2$]/[M$_1$]. The intercept of straight lines A(X) multiplied by [M$_1$] gives values of Rp(f), and from the equation Rp=Rp(f) + Rp(CT), RP(CT) was calculated.

The relative participation of Rp(f) and RP(CT) as percent of total initial rate of copolymerization and the influence of monomer concentration in feed is presented in Table 2.

It is evident that in the copolymerization of PhOPhMI with St, the Rp(f) is higher than Rp(CT), while in the copolymerization with sterically hindered (αMeSt and βMeSt the propagation through RP(CT) predominates. It is in agreement with the results previously obtained for a large number of copolymerizations which proceed through the participation of CT-complex monomers.

CONCLUSION

1.   N(p-Phenoxy-phenyl)maleimide (PhOPhMI) was prepared by cyclization of the corresponding maleamic acid.

2.   Homopolymerization of PhOPhMI and copolymerization with St, (MeSt and (MeSt was performed in the presence of AIBN and it was found that alternating copolymers were obtained under different monomer-to-monomer ratios in the feed.

3.   It was further found that the formation of alternating copolymers can be best explained by the mechanism based on the participation of CT-complex monomers.

4.   Homopolymer and copolymers are thermally stable up to 350°C under the TGA conditions. Tgs and higher transition temperatures are within the thermally stable region.

ACKNOWLEDGEMENTS

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