Alternating Copolymerization and Copolymers of Styrene and *N*-(2,4-Dibromophenyl)maleimide

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Free radical copolymerization of styrene (St) and *N*-(2,4-dibromo-phenyl)maleimide (DBPMI) in dioxane solution gave an alternating co-polymer in all proportions of feed comonomer compositions. The copolymerization reactivity ratios were found to be $r_1 = 0.049 \pm 0.0023$ (St) and $r_2 = 0.0115 \pm 0.0018$ (DBPMI); Q and e values were also calculated. The molecular weights of the copolymers obtained are relatively high and the alternating copolymer had a glass transition temperature of 507 K: the thermal stability of the copolymer is higher than that of polystyrene.

The equilibrium constant of charge-transfer complex of St and DBPMI was determined by ^{1}H-NMR spectroscopy in deuterated chloroform and gave a value of 0.12 L/mol. The initial rate of copolymerization was measured as a function of the monomer ratios, and the participation of the charge-transfer complex monomer and the free monomers was quantitatively estimated. It was established that the copolymerization of St with DBPMI proceeds predominasntly through participation of the free monomers.

INTRODUCTION

Free radical copolymerization of *N*-substituted maleimides with vinyl monomers have been reported in many papers. It was shwon that their reactivity strongly depended on the polarity of the comonomer used.[1–3] In all cases of styrene copolymerizations a nearly alternating copolymerization took place and gave random placement of the monomers. These polymers are characterized by a rigid volume structure and high thermal stability and they also have unique properties like optical and catalytic activities.[4,5]

Some work dealing with copolymerization of brominated *N*-phenylmaleimides also showed that these monomers readily formed copolymers of nearly alternating structures with styrene and butadiene[6,7] and gave random copolymers with methyl acrylate, methyl methacrylate and acrylnitrile.[8,9]

Several approaches have been used in the literature to treat the kinetic data of the alternating copolymerization system with the anticipated participation of a

charge-transfer complex (CTC) formed between two monomers.[10-13] However, Rätzsch and Vogl[14] examined in great detail the copolymerization of maleic anhydride with a series of donor monomers and concluded that CTC does not play a significant role in the kinetics of the reaction.

The treatment proposed by Shirota et al.[15] assumes that alternation in the resulting copolymers is brought about by stabilization of the transition state in cross reactions of the free monomers and the CTC. This kinetic treatment has been adopted also in the present paper.

In continuation of our studies on brominated N-phenylmaleimide copolymers,[7,9,16,17] we have shown that in the copolymerization of styrene with N-(4-bromophenyl)maleimide[17] and N-(2,4,6-tribromophenyl)maleimide,[7] in all proportions of comonomers in the feed, there is a strong tendency towards alternation. The present report deals with the copolymerization kinetics of N-(2,4-dibromophenyl)maleimide (DBPMI) with styrene in dioxane using 2,2'-azobis(isobutyronitrile) (AIBN) as initiator; the polymerization was followed by dilatometry. The participation of the CTC monomer and the free monomers in the initial rate of copolymerization was quantitatively estimated. Measurements of some characteristic properties of the copolymers were also made.

EXPERIMENTAL

Materials

Styrene and solvents were purified by distillation prior to use. N-(2,4-Dibromophenyl)maleimide was prepared in 75% yield in a two stage synthesis from maleic anhydride and 2,4-dibromoaniline;[18] it was twice recrystallized from ethanol, m.p. 106–107 °C. The ^{1}H-NMR spectrum in $CDCl_3$ showed a singlet at 6.89 ppm (maleic) and the following signals for the phenyl ring: C-3, singlet at 7.90 ppm; C-5, doublet at 7.60 ppm; C-6, doublet at 7.10 ppm. 2,2'-Azobis(isobutyronitrile) was recrystallized from methanol.

Measurements

Thermogravimetric analyses (TGA, DTG) were carried out with a Perkin-Elmer TGS-2 and DSC-7 instrument in a helium and air atmosphere at a heating rate of 20 °C/min. ^{1}H-NMR spectra were measured on a 90-MHz Varian EM-90 Spectrometer in deuterated chloroform with TMS as the internal standard. The composition of copolymers was established by bromine and carbon analyses. Molecular weights of the copolymers were measured by gel permeation chromatography carried out on an Aerograph 8500 Varian instrument fitted with a UV detector. Styragel columns (Waters Associates) were used at a flow rate of 1 mL/min of degassed tetrahydrofuran. Retention times were calculated on polystyrene equivalents.

The equilibrium constant of St and DBPMI complexation was determined by the ^{1}H-NMR continuous variation method in deuterated chloroform at 35 °C with TMS as the internal reference.[19,20]

Polymerization Procedures

Solution polymerization to low conversion was carried out in dioxane (50 mL solutions) with monomers (0.025 mol) and AIBN (0.082 g) as initiator at 50 °C. Polymerization were carried out under a constant stream of nitrogen in a 100 mL, double-jacketed glass reactor equipped with a magnetic stirrer. After an appropriate time interval (10–100 min), the sample was withdrawn and the solution precipitated in methanol, the polymer was isolated by filtration, dissolved in dioxane, reprecipitated, and dried at 60 °C and 0.1 mm.

Rates of copolymerization were measured dilatometrically. Dilatometers (about 20 mL) filled with the dioxane solution of monomer mixture, and initiator (AIBN) were connected to a high vacuum line and freed of oxygen by three freezing-thawing cycles. The dilatometers were then placed in thermostat bath and the volume contraction was recorded as a function of time. The reaction was terminated by vacuum suction of the contents from the dilatometers and the polymer from the reaction mixture precipitated in excess cold methanol. The polymerization conversion was determined gravimetrically.

RESULTS AND DISCUSSION

Free radical copolymerization of styrene (St) with N-(2,4-dibromophenyl)maleimide (DBPMI) was performed in dioxane solution using 2,2'-azobisisobutyronitrile (AIBN) as initiator. The influence of the mole fraction of the DBPMI in the initial monomer mixture (f) on the composition (F) and some properties of the copolymers obtained for low conversions are summarized in Table I. The plot of instantaneous

TABLE I.

Copolymerization of styrene (M_1) and N-(2,4-dibromophenyl)maleimide (M_2) in dioxane solution at low conversions[a]

f_2[b]	Conversion %	Br %	F_2[c]	$\bar{M}_w$[d] $\times 10^{-3}$	$\bar{M}_n$[e] $\times 10^{-3}$	T_g[f] °C
0.10	11.3	33.02	0.404			
0.20	8.2	35.04	0.453	51.0	23.3	223.2
0.30	7.6	35.76	0.472	69.0	19.4	
0.40	5.0	36.17	0.483			230.9
0.50	6.3	36.46	0.491	76.2	31.7	232.3
0.60	7.9	36.67	0.497			233.8
0.70	9.1	36.88	0.503	87.9	47.2	
0.80	4.4	37.12	0.510			
0.90	8.8	37.73	0.528			

[a] Polymerization conditions: Dioxane solution (50 mL) of monomers (0.025 mol) and AIBN (0.082 g), 50 °C.

[b] Mole fraction of DBPMI in the initial monomer mixture.

[c] Mole fraction of DBPMI in copolymer.

[d] Weight-average molecular weight determined by means of gel-permeation chromatography (solvent tetrahydrofuran).

[e] Number-average molecular weight determined by means of gel-permeation chromatography (solvent tetrahydrofuran).

[f] Glass transition temperature determined by means of differential scanning calorimetry.

copolymer composition (Figure 1) shows a marked tendency towards alternating composition, the composition of the copolymer being almost equimolar regardless of the monomer feed composition. By using the Kelen-Tüdös integral methods, the copolymerization reactivity ratios[21] and the confidence interval[22] were calculated and also presented graphically using the least-squares method (Figure 2). They have been related to the polarity (e) and the resonance effect (Q) in the Alfrey-Price
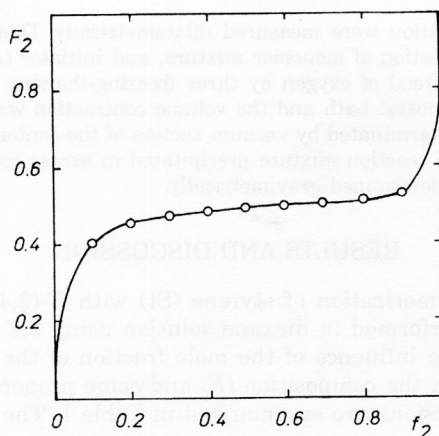
Figure 1. Monomer-copolymer composition curve for the copolymerization of styrene (M_1) with N-(2,4-dibromophenyl)maleimide (M_2) in dioxane at 50 °C with AIBN as initiator. Mole fraction of M_2 in copolymer F_2 vis. mole fraction of M_2 in initial monomer mixture f_2.

scheme based on the arbitrarily chosen reference values of $Q = 1$ and $e = -0.80$ for styrene.[23] The values $r_1 = 0.049 \pm 0.023$ ($M_1 = $ St) and $r_2 = 0.0115 \pm 0.0018$ ($M_2 = $ DBPMI) and $e_2 = 1.94$ and $Q_2 = 2.29$ were obtained. It is well documented that monomers with such a large e value posses electron-acceptor properties in combination with electron-donor monomers, of which styrene is a typical example. They readily form alternating copolymers in conventional free radical polymerization.[24] The tendency to form an alternating St/DBPMI copolymer is also verified by the monomer-
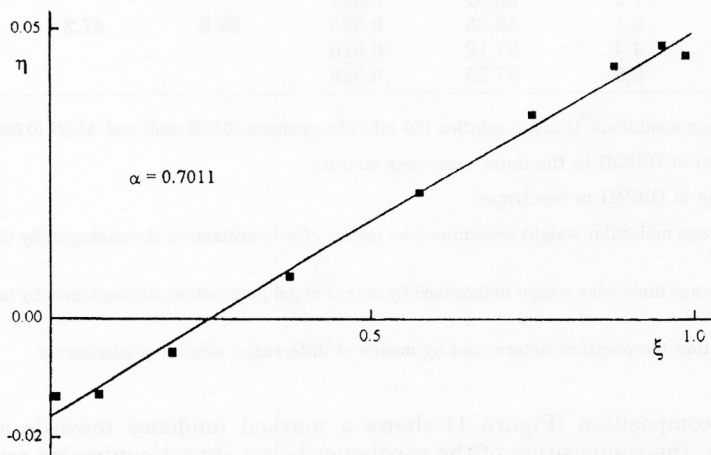

Figure 2. Kelen-Tüdös diagram for the calculation of copolymerization reactivity ratios r_1, r_2 for the system styrene (M_1) and N-(2,4-dibromophynel)maleimide (M_2) in dioxane. For the straight line, r_1 and $- r_2/\alpha$ are the values of η for $\xi = 1$ and $\xi = 0$, respectively.
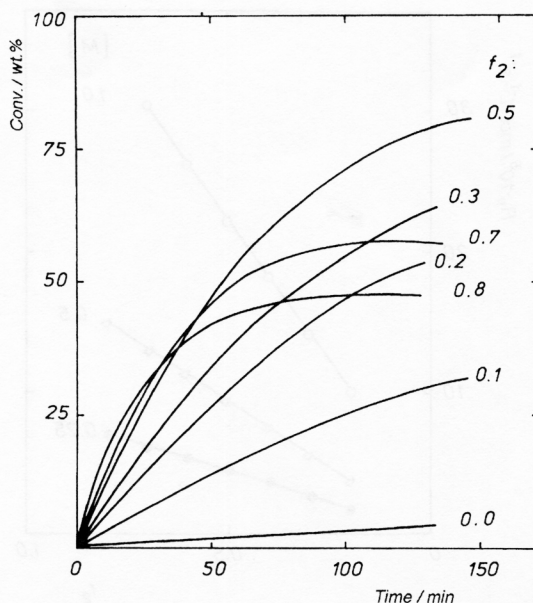
Figure 3. Influence of mole fraction of M_2 in initial monomer mixture f_2 (numerical values at curves) on conversion $vis.$ reaction time curves in copolymerization of styrene (M_1) and N-(2,4-dibromophenyl)maleimide (M_2) at 60 °C; total monomer concentration $[M]$ = 0.5 mol/L, [AIBN] = $1 \cdot 10^{-2}$ mol/L, in dioxane.

copolymer composition diagram presented in Figure 1. The values of the glass transition temperature (T_g) of the copolymers (Table I) have found to be in the range of 223 to 234 °C, in spite of large differences in the monomer feed composition, regarding the alternating composition of the copolymers.

The course of the polymerization up to high conversions is represented by the integrated time − conversion curves (Figure 3). It is clearly evident that, in spite of the initial polymerization rate increasing by increasing the DBPMI content in the monomer feed, the highest conversion was obtained at equimolar monomer amounts in the monomer mixture. Such behaviour is a common characteristic of alternative copolymerization systems.[10–15]

To illustrate the role of the CTC monomer in ithe copolymerization process, the initial rates were measured for various feeds but at total monomer concentrations of 0.25, 0.50. and 1.0 mol/L, respectively, as shown in Figure 4. These initial rates were determined by dilatometry at low conversions, and they gave straight lines in all concentrations. Figure 5 shows that the initial rate of copolymerization was proportional to the square root of the initiator (AIBN), which demonstrates the bimolecular termination reactions.[23] In the case of bimolecular termination, the following equations were derived by Shirota et $al.$[15] to quantify the degree of participation of the free monomers and the CTC monomer in the copolymerization reaction:
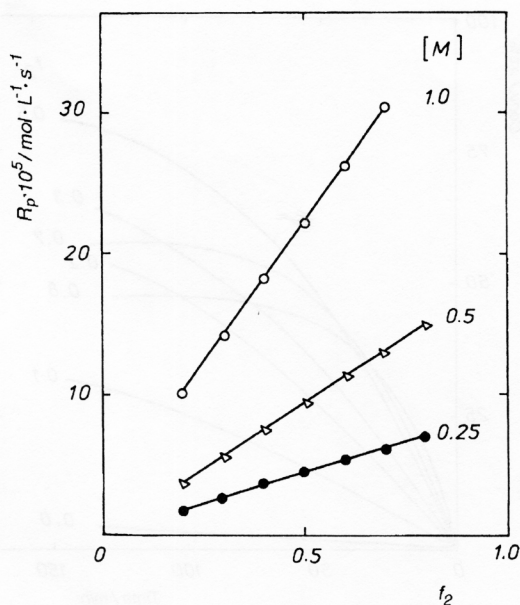
Figure 4. Dependence of the initial reaction rate, R_p, on the mole fraction of M_2 in initial monomer mixture f_2 of the copolymerization of styrene (M_1) and N-(2,4-dibromophenyl)maleimide (M_2), for various total monomer concentrations of [M] = 0.25, 0.5 and 1.0 mol/L, concentration of [AIBN] = $1 \cdot 10^{-2}$ mol/L, in dioxane at 60 °C.
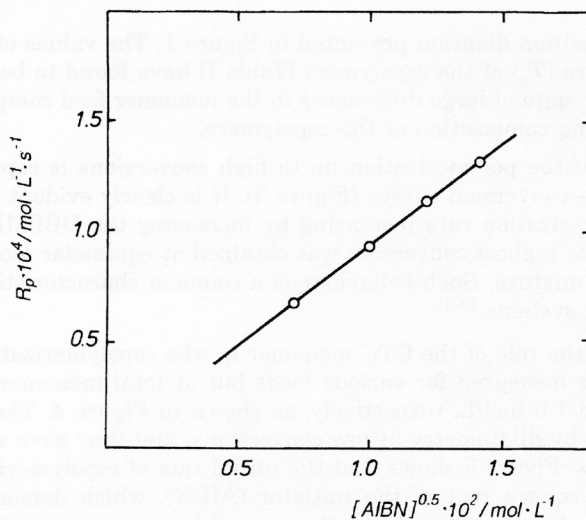

Figure 5. Dependence of the inital rate of copolymerization, R_p, of styrene (M_1) and N-(2,4-dibromophenyl)maleimide (M_2) on AIBN $^{0.5}$ for the total monomer concentration [M] = 0.5 mol/L and [M_1] = [M_2] = 0.25 mol/L, in dioxane at 60 °C.

$$R_p = A(X) \, K \, \{k_{1c}/k_{12} + (k_{2c}/k_{21}) \, X\} \, [M_1]^2 + A \, (X) \, [M_1] \tag{1}$$

$$R_p(f) = A \, (X) \, [M_1] \tag{2}$$

$$R_p(CT) = A(X) \, K \, \{k_{1c}/k_{12} + (k_{2c}/k_{21}) \, X\} \, [M_1]^2 \tag{3}$$

$$A(X) = \frac{2k_{21}k_{12}R_i^{1/2}X}{(k_{t11}k_{21}^2 + 2k_{t12}k_{21}k_{12}X + k_{t22}k_{12}^2X^2)^{1/2}} \tag{4}$$

$$R_i = 2k_d fI$$

$$[M_2] = X \, [M_1]$$

$$R_p \, / \, [M_1] = A \, (X) \, K \, \{k_{1c}/k_{12} + (k_{2c}/k_{21}) \, X\} \, [M_1] + A \, (X) \tag{5}$$

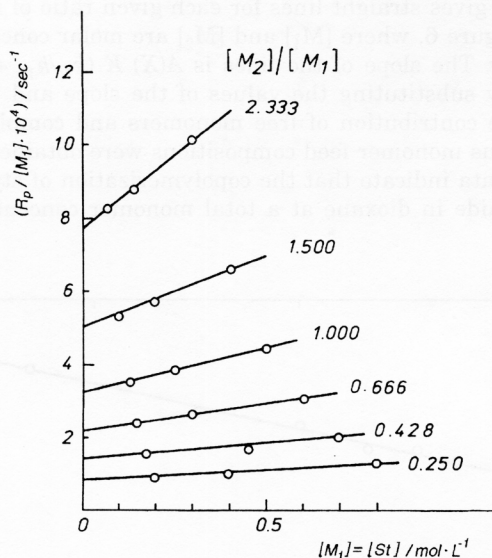$$F \, (X) = K \, \{k_{1c}/k_{12} + (k_{2c}/k_{21}) \, X\} \tag{6}$$

Figure 6. Dependence of the ratio of the initial reaction rate and styrene concentration, R_p / [St] on [St] at various monomer feed ratios in the copolymerization of styrene (M_1) and N-(2,4-dibromophenyl)maleimide (M_2), for the total monomer concentration of [M] = 0.25, 0.5, and 1.0 mol/L, [AIBN] = 1 · 10^{-2} mol/L in dioxane at 60 °C.
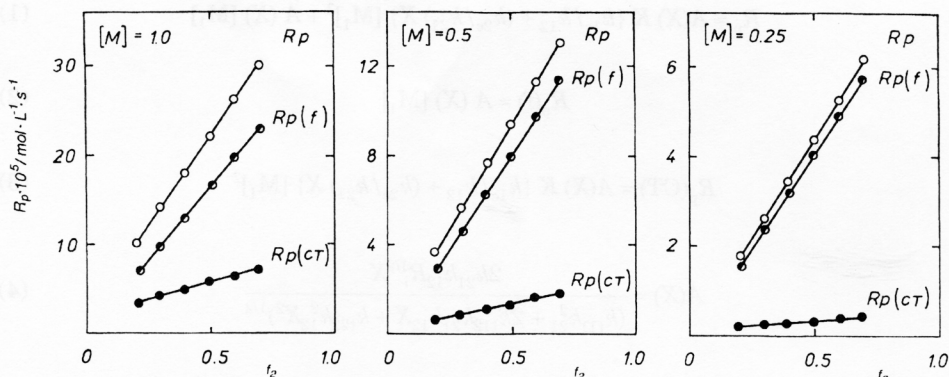
Figure 7. Relative participation of free (*f*) and complexed (CT) monomers in the rate of copolymerization (R_p) of styrene (M_1) and *N*-(2,4-dibromophenyl)maleimide (M_2) at different monomer feed concentrations in dioxane at 60 °C.

Here, X is the monomer feed molar ratio as represented above, K is the equilibrium constant for the CTC monomer formation, and k_{t11}, k_{t22} and k_{t12} are the rate constants for the bimolecular, homo and crosstermination reactions of growing polymer radicals, respectively. The overall initial rate R_p is the superposition of the reaction rates of the free monomer $R_p(f)$ and of the CTC monomer $R_p(CT)$. The plot of $R_p/[M_1]$ against $[M_1]$ gives straight lines for each given ratio of monomer concentration, as shown in Figure 6, where $[M_1]$ and $[M_2]$ are molar concentrations of St and DBPMI, respectively. The slope of the lines is $A(X) K (k_{1c}/k_{12} + k_{2c}/k_{21})X$ and their intercept is $A(X)$. By substituting the values of the slope and the intercept in the above equations, the contribution of free monomers and complexed monomer as a function of the various monomer feed compositions were obtained and are presented in Figure 7. These data indicate that the copolymerization of styrene and *N*-(2,4-dibromophenyl)maleimide in dioxane at a total monomer concentration of 0.25, 0.50
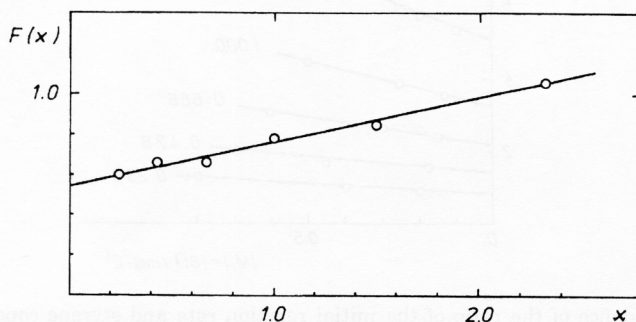

Figure 8. Plot of $F(X) = K \{k_{1c}/k_{12} + (k_{2c}/k_{21}) X\}$ *versus* the monomer feed molar ratio (X) in the copolymerization of styrene (M_1) and *N*-(2,4-dibromophenyl)meldimide (M_2) in dioxane at 60 °C.

and 1.0 mol L^{-1}, proceeds predominantly via cross propagation of free monomers but that increasing monomer concentrations promote the participation of the CTC monomer. The average contribution of $R_p(CT)$ calculated from Figure 7 is 8.3% (0.25 M), 15.4% (0.50 M) and 26.6% (1 M). From Eq. (6) it is possible to get a qualitative estimation of the relative reactivity between the St-DBPMI complex and the free monomers. Numerical values of the reactivity ratios determined from the intercept and slope of the straight line in Figure 8 are $K(k_{1c}/k_{12}) = 0.54$ and $K(k_{2c}/k_{21}) = 0.22$, respectively; and the ratio $(k_{1c} \cdot k_{21}) / (k_{2c} \cdot k_{21}) = 2.45$.
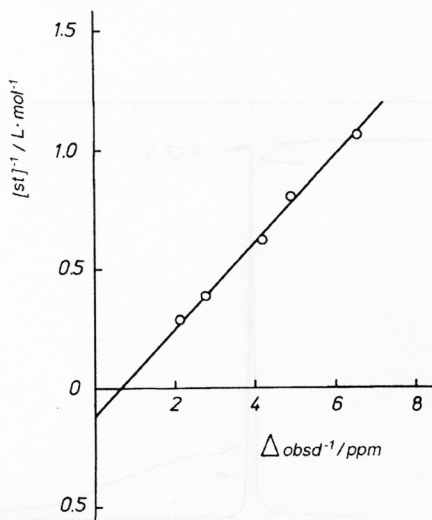

Figure 9. Plot of Δ_{obsd}^{-1} *vis.* $1/[St]_o$ for the ^{1}H-NMR shifts of N-(2,4-dibromophenyl)maleimide olefinic protons in the presence of styrene (St) as electron donor in deuterated chloroform, at 35 °C.

The formation of CTC between monomers was proved by ^{1}H-NMR spectroscopy; the equilibrium constant of complex formation (K) was determined by the Hanna and Ashlaugh method.[19] The change of the position of DBPMI olefinic proton, which appeared at 6.89 ppm in deuterated chloroform, was monitored as a function of St concentration. A noticeable change was observed of the chemical shift value on increasing the St concentration from 0.97 to 3.55 mol/L, while the concentration of DBPMI was very small (0.08 mol/L) and kept constant. Constant K was calculated from the intercept of the straight line (Figure 9) by applying the following equation:

$$1/[D_o] = K \cdot \Delta_{compl} \cdot (1/\Delta_{obsd}) - K \qquad (7)$$

where $[D_o]$ is the concentration of St, $\Delta_{obsd} = \delta_{fr} - \delta_{obsd}$, $\Delta_{compl} = \delta_{fr} - \delta_{compl}$, δ_{fr} is the chemical shift of the free DBPMI, δ_{obsd} are chemical shifts of DBPMI in the presence

of different concentrations of St, and Δ_{compl} is the chemical shift of the complexed DBPMI. The numerical value of K obtained by the least-squares method is 0.12 L/mol.

By substituting the value of K, the following values of the relative relationship between the propagation reaction constants of the complexed and free monomers can be estimated: $k_{1c} = 4.5\ k_{12}$ and $k_{2c} = 1.8\ k_{21}$. These results showed that the propagation rates of complexed monomer of styrene radicals is greater than that of DBPMI radicals. However, the strong tendency toward alternating copolymerization of the St-DBPMI system indicates that the St free radicals are preferentially formed through complex addition whose concentration, under the experimental conditions used, is relative small.
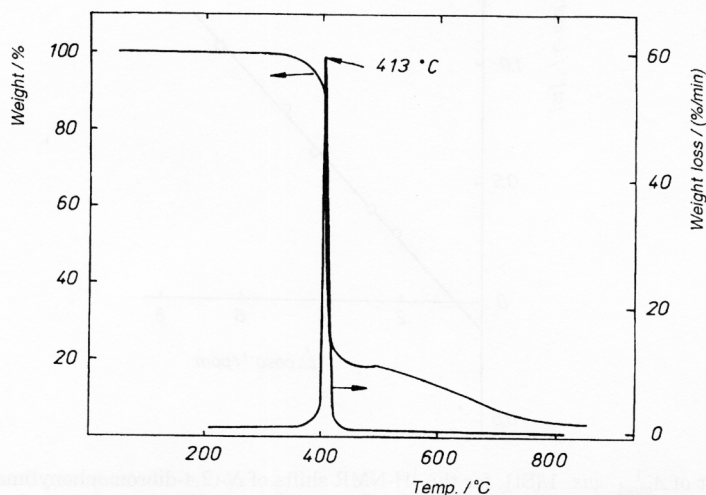

Figure 10. Thermogravimetry and derivative thermogravimetry curves of the laternating copolymer of styrene and N-(2,4-dibromophenyl)maleimide in helium.

The thermal stability of St-DBPMI alternating copolymer was determined by means of thermogravimetry (TG) and differential thermal analysis (DTA) in helium atmosphere (Figure 10). The obtained curves show that the copolymer starts to decompose spontaneously at 390 °C, which is about 30 °C above the decomposition temperature of polystyrene. Some residue (14.5 wt.%) at the end of the fast decomposition indicates that depolymerization to volatile product did not proceed to completion, which is typicaly characteristic of halogenated N-phenyl maleimide copolymers.[25]

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SAŽETAK

Alternirajuća kopolimerizacija i kopolimeri stirena i N-(2,4-dibromofenil)maleimida

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Reakcijom kopolimerizacije stirena (St) i N-(2,4-dibromofenil)maleimida (DBPMI) u otopini dioksana, iniciranom slobodnim radikalima, nastaje alternirajući kopolimer pri svim sastavima smjese monomera. Omjeri reaktivnosti monomera određeni pri niskim konverzijama iznose: $r_1 = 0.049 \pm 0.023$ (St) i $r_2 = 0.015 \pm 0.018$ (DBPMI), a izračunane su i vrijednosti za Q i e. Dobiveni kopolimeri su relativno visokih molekulskih masa, staklište alternirajućeg kopolimera iznosi 507 K, a termička stabilnost mu je veća nego polistirenu.

Metodom ¹H-NMR utvrđeno je da St i DBPMI stvaraju kompleks (konstanta ravnoteže $K = 0,12$ L/mol). Početna brzina reakcije kopolimerizacije linearno se povećava s povećanjem udjela DBPMI u početnoj smjesi monomera, a kvantitativno je određen i doprinos kompleksirajućeg monomera i slobodnih monomera na ukupnu brzinu reakcije. Reakcija kopolimerizacije stirena i DBPMI odvija se pretežno uz sudjelovanje slobodnih monomera.