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Alternating Copolymers of beta-Alkoxystyrenes and *N*-Phenylmaleimide

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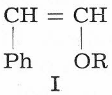
Alternating copolymers of beta-alkoxystyrenes (I) and *N*-phenylmaleimide (NPMI) were prepared by free-radical initiated polymerization in bulk or in toluene as solvent. The equilibrium constants of I (R = Et and *sec*-Bu) and NPMI were determined by the transformed Benessi-Hildebrand NMR method in $CDCl_3$, and it was found that the bulkiness of alkyl group has no significant influence on the equilibrium constants. The rate of copolymerization, however, was largely dependent on the bulkiness of alkyl group, and rate constants decreased by increasing the size of alkyl group. It was further found that the weight loss in the thermo-gravimetric analysis increases by the increase of bulkiness of alkyl group in electron donor monomer. The linear correlation between the logarithm of rate constants of k_{Me} over k_R against Taft-Hancock steric constants and the parallelism between weight loss values in thermograms and steric factors of respective alkyl groups indicate that the rate of copolymerization and thermal degradation are sterically controlled processes.

INTRODUCTION

In continuation of our studies on the preparation of alternating copolymers via the participation of charge-transfer-complex (CTC) monomers, we prepared a series of copolymers of beta-alkoxystyrenes (I) and *N*-phenylmaleimide (NPMI)



$$\underset{Ph}{CH} = \underset{OR}{CH}$$

I

R = Me, Et, *n*-Pr, *n*-Bu, *iso*-Pr, *sec*-Bu

The copolymerization was performed in bulk or in toluene using AIBN as initiator, and it was found that alternating copolymers are obtained regardless of the monomer-to-monomer feed ratio. The presence of CTC monomers was proved by the characteristic chemical shift of ethylene protons in NMR spectra. By applying the transformed Benessi-Hildebrand NMR method the equilibrium constants of copolymers were determined. It was further found that the rate of copolymerization depends on the bulkiness of alkyl group in electron donor monomer I and that by increasing the size of alkyl group the rate of copolymerization decreases. The numerical values of rate constants in the copolymerization of I and II coincide with Taft-Hancock steric parameters, thus indicating that the rate of copolymerization is sterically controlled.

The copolymers are soluble in methyl ethyl ketone and are stable up to 300 °C, as indicated by thermogravimetric analysis. It is interesting to note that the thermal decomposition of copolymers is also a sterically controlled reaction.

EXPERIMENTAL

Materials

Monomers I were prepared by condensation of phenylacetylene with the corresponding sodium alcoholates and were purified by fractional distillation, as previously described.[1] *N*-Phenylmaleimide was a commercial product (Aldrich Europe), m. p. 85—87 °C, and was used as received without purification.

Polymerization Procedure

Polymerizations were carried out in vacuum sealed 10-ml glass vials which were thoroughly degassed before sealing, and placed into an oil bath thermostated to the desired temperature. The reaction product was dissolved in methyl ethyl ketone and precipitated with methanol, yielding a white powdery product. When polymerization was performed in toluene, the copolymer was separated by precipitation from toluene solution with methanol.

Physicochemical Measurements

NMR spectra were obtained on a Varian EM 390 NMR spectrometer. The equilibrium constants of the CTC monomers of I (R = Et or *sec*-Bu) with NPMI were determined in deuterated chloroform, TMS being used as an internal reference. The concentration of NPMI was 0.1 mol/litre and the chemical shift 6.83 ppm, while the concentration of I varied from 0.5 to 2 mol/litre. Molecular weights were determined on a Varian HPGPC Model 5800 using a set of 4 Styrogel columns with THF as solvent. The average molecular weights were calculated by calibrations with standard polystyrenes of known molecular weights. Glass transition temperature measurements were carried out using a Perkin-Elmer Differential Scanning Calorimeter Instrument Model DSC-2. The scanning rate was 20 °C/min in nitrogen. Thermograms of copolymers were determined on a Perkin-Elmer TGS-2 Thermogravimetric System in the temperature range of 50—600 °C at a heating rate of 10 °C/min in nitrogen or in air.

RESULTS AND DISCUSSION

It was shown in previous papers that beta-alkoxystyrenes (I) do not homopolymerize by free radical initiators but that they readily copolymerize with maleic anhydride under the normal conditions of free radical polymerization and that copolymerization proceeds under participation of the charge-transfer-complex monomers.[1,2] The same was also found in this paper when I was copolymerized with NPMI. On admixture of I to NPMI no change of colour was observed. However, in contrast to the findings of Barrales-Rienda et. al.[3] and Yaskihara et. al.[4] that no complex formation between styrene and NPMI was observed by NMR spectroscopy, we found that in case of I and NPMI the equilibrium constant can easily be determined by the transformed Benessi-Hildebrand NMR method in deuterated chloroform. The concentration of NPMI was constant and very small, 0.1 mol/litre, so that self association could be neglected, while the concentration of I (R = Et or *sec*-Bu) varied from 0.5 to 2 mol/litre.

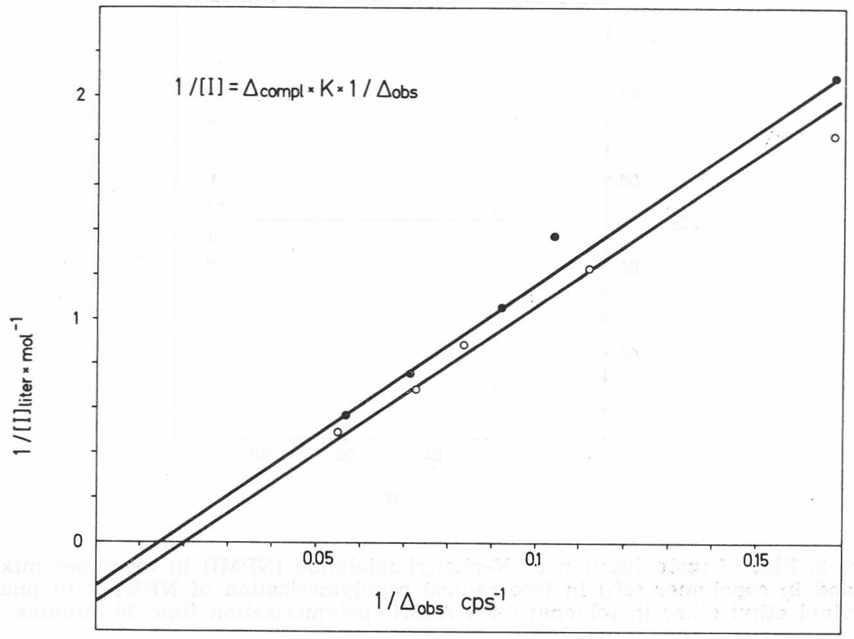


Figure 1. Reciprocal values of molar concentration of phenylvinyl alkyl ethers (I) against reciprocal values of the difference of chemical shifts in NMR of complexed and uncomplexed *N*-phenylmaleimide (NPMI). (○) I (R = Et); (●) I (*R* = *sec*-Bu); 35 °C in $CDCl_3$; NPMI = 0.1 mol/litre; I (R = Et or *sec*-Bu) = 0.5 to 2 mol/litre.

Figure 1 shows the plot of the reciprocal of molar concentration of I (R = Et or *sec*-Bu) against the reciprocal of chemical shifts of complexed and uncomplexed NPMI molecules. The equilibrium constants were calculated from the intercept of the straight lines and had the values of 0.28 litre/mol for I (R = Et) and 0.2 litre/mol for I (R = *sec*-Bu) with NPMI; this indicates that a considerable amount of complex exists in the copolymerization system.

It is known that NPMI can homopolymerize by free radical initiated mechanism but in the copolymerization of NPMI with I, at various I to NPMI ratio in the feed, the alternating copolymers were obtained as shown in Figure 2. The copolymer composition was determined by elemental analysis.

Properties of copolymers are shown in Table I.

The data in Table I indicate that the molecular weight of copolymers decreases by increasing the size of alkyl group, while the loss of weight in thermogravimetric analysis increases by increasing the effective bulkiness of alkyl group in the electron donor molecule. It is evident that all copolymers are stable in nitrogen up to 300 °C.

The rate of copolymerization of I with NPMI is shown in Figure 3. The copolymerization was performed in toluene at 70 °C using AIBN as initiator. It is obvious that the rate of conversion decreases with the increase of bulkiness of alkyl group in the electron donor monomer. By assuming that the

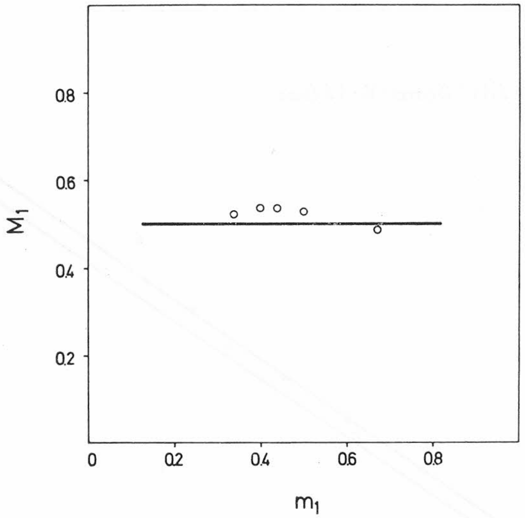
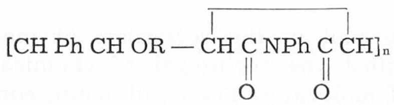


Figure 2. Plot of mole fraction of *N*-phenylmaleimide (NPMI) in monomer mixture (m_1) and in copolymer (M_1) in free radical copolymerization of NPMI with phenylvinyl ethyl ether in toluene; 0.4% AIBN; polymerization time 30 minutes.

TABLE I

Molecular Weights, Glass Transition Temperature, and Loss of Weight at 300 °C and 400 °C in TGA of



$$[\mathrm{CH\,Ph\,CH\,OR} - \mathrm{CH}\,\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\,\mathrm{NPh}\,\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\,\mathrm{CH}]_n$$

				Loss of Weight, %		in Air	
R	$\overline{M}_w \times 10^3$	$\overline{M}_n \times 10^3$	T_G °C^5	300 °C	400 °C	300 °C	400 °C
					in Nitrogen		
Me	133.3	63.2	278	0.9	35.0	0.05	66.0
Et	116.5	55.0	258	2	45.3	1.5	66.0
n-Pr	91.0	44.3	250	1	52.7	1.5	72.5
n-Bu	81.0	39.0	240				
iso-Pr	36.0	17.0	271	1.8	57.0	1.6	69.0
sec-Bu	23.6	11.0	252	2	59.0	5	67.6

concentration of the complex is small in comparison with the total monomer concentration, and since at different monomer-to-monomer feed ratio alternating copolymers are formed, the reaction can be considered as a pseudo-first order reaction, so that the plot of ln $[M_o]/[M_t]$ against time should be linear (Figure 4). Rate constants of the copolymerization of I and NPMI were determined as slopes of the straight lines in Figure 3: $k_{Me} = 0.012$, $k_{Et} = 0.0092$, $k_{n\text{-}Pr} = 0.0066$, $k_{n\text{-}Bu} = 0.0056$, $k_{iso\text{-}Pr} = 0.0035$, $k_{sec\text{-}Bu} = 0.002$ min^{-1}. As evident from these data, an important factor determining the rate of copolymerization of I and NPMI is the steric character of alkyl group in I. Figure 5 shows the plot of log k_{Me}/k_R against modified Taft-Hancock steric factors E_s^c for alkyl group attached to ether group in the electron donor molecule. E_s^c was calculated according to the procedure outlined by Fujita and coworkers.[6,7]

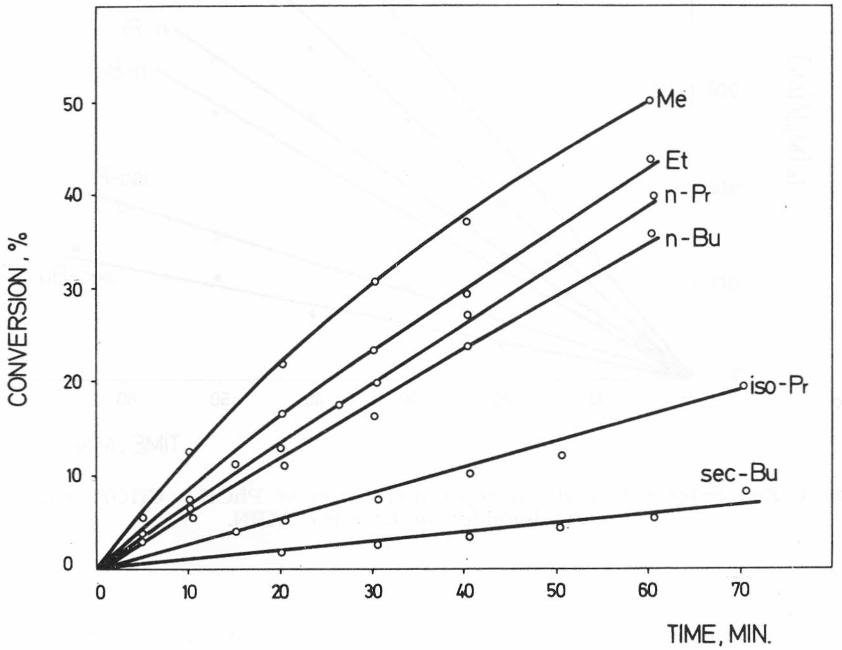


Figure 3. Time-conversion curves in copolymerization of PhCH = CHOR and N-phenylmaleimide 70 °C; 0.4% AIBN; in toluene solution.

The linear correlation between the logarithm of rate constants of k_{Mc} over k_R against Taft-Hancock steric constants indicates that the copolymerization of I and NPMI is a sterically controlled reaction. It should be, however, pointed out that the relatively large scattering of results in Figure 5 is a consequence of the relatively low reproducibility in gravimetric point-by-point method used in the determination of rate constants at low conversion.

Similar to the findings previously described for the thermal decomposition of poly[phenylvinyl alkyl ethers (or thioethers) -co-maleic anhydride],[8] Figure 6 indicates that the rate of weight loss in thermogravimetric analysis largely depends on the steric characteristic of alkyl substituent in the electron donor moiety of poly(phenylvinyl alkyl ether-co-N-phenylmaleimide). It is evident

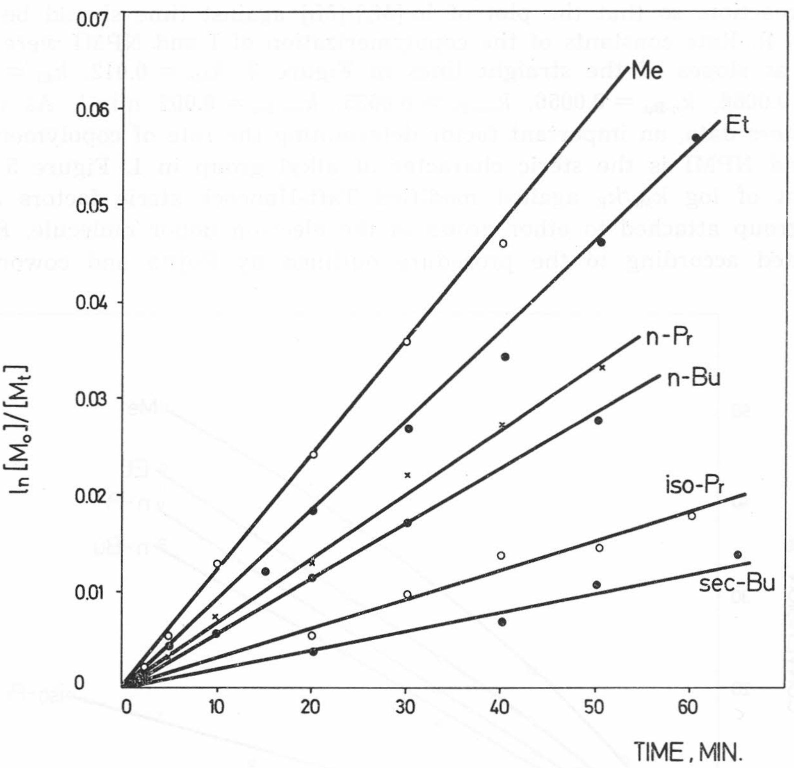


Figure 4. Fist order rate plots in copolymerization of PhCH = CHOR with *N*-phenylmaleimide; 70 °C; 0.4% AIBN.

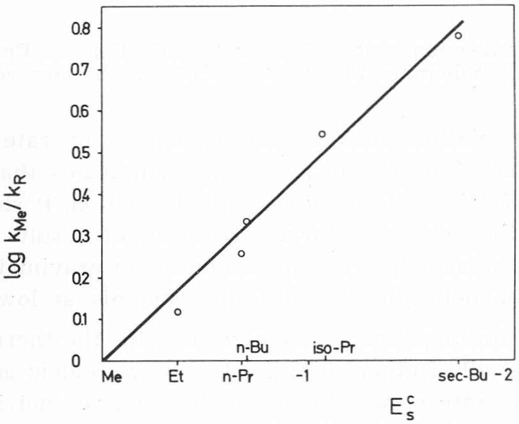
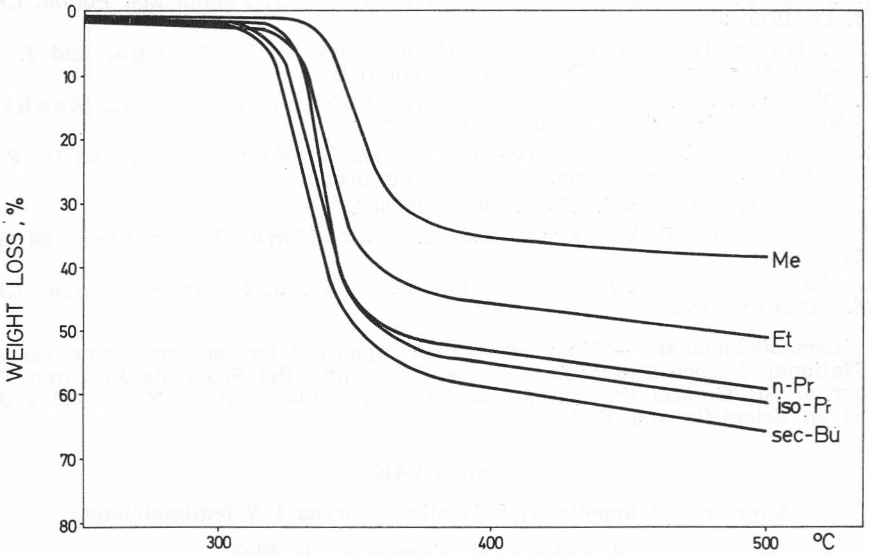


Figure 5. Plot of log k_{Me}/k_R against Taft-Hancock steric factors E_s^c in bulk copolymerization of PhCH =CHOR and *N*-phenylmaleimide; 70 °C; 0.4% AIBN.

from Figure 7 that at 400 °C the rate of weight loss increases in the following order:



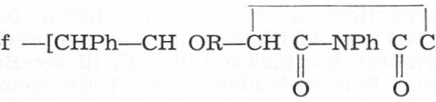


Figure 6. Thermogram of $-[\mathrm{CHPh{-}CH(OR){-}CH{-}C(=O){-}NPh{-}C(=O){-}CH}]-_n$

heating rate 10 °C/min in nitrogen.

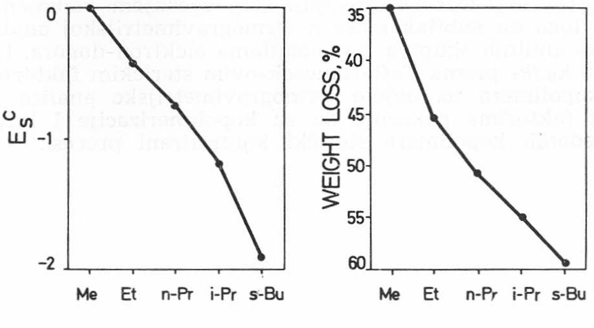


Figure 7. A comparison of Taft-Hancock steric constants E_s^c and the weight loss in thermogravimetric analysis of poly(phenylvinyl alkyl ethers-co-*N*-phenylmaleimide).

Me<Et<*n*-Pr<*iso*-Pr<*sec*-Bu. The data in Figure 7 show a parallelism between weight loss values in thermograms of alternating copolymers of I and NPMI and steric factors of the respective alkyl groups, thus indicating that the thermal decomposition of the studied copolymers under the TGA conditions is also a sterically controlled process.

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SAŽETAK

Alternirajući kopolimeri beta-alkoksistirena i *N*-fenilmaleimida

R. Vuković, V. Kurešević i D. Fleš

Kopolimerizacijom u masi ili u toluenu fenilvinil-alkil-etera I i *N*-fenilmaleimida (PMI) uz AIBN kao inicijator priređeni su alternirajući kopolimeri. Konstante ravnoteže kompleksa I (R = Et ili *sec*-Bu) sa NPMI određene su primjenom modificirane Benessi-Hildebrandove NMR metode u $CDCl_3$, te je nađeno da konstante ravnoteže ne ovise bitno o volumenu alkilne skupine u elektron-donorskom monomeru; $K_{R=Me} = 0,28$ l/mol; $K_{R=sek\text{-}Bu} = 0.20$ l/mol. To dokazuje da CT kompleks nastaje putem vinilnih skupina, a ne putem etera. Dok konstante ravnoteže nisu ovisne o steričkim faktorima, brzina kopolimerizacije bitno ovisi o volumenu alkilne skupine. Konstanta ravnoteže se smanjuje s povećanjem volumena alkilne grupe. Nađeno je osim toga da gubitak mase u termogravimetrijskoj analizi raste s povećanjem volumena alkilnih skupina u molekulama elektron-donora. Linearna ovisnost odnosa logaritma k_{Me}/k_R prema Taft-Hancock-ovim steričkim faktorima i paralelizam gubitka mase kopolimera uz uvjete termogravimetrijske analize s Taft-Hancock-ovim steričkim faktorima pokazuje da su kopolimerizacije I i NPMI i termička razgradnja priređenih kopolimera sterički kontrolirani procesi.