Substituted Styrenes-Maleic Anhydride Copolymers-Measurements of the Reactivity Ratios with High Conversions and Relations between Molecular Masses and Viscosity

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ABSTRACT: Three substituted styrenes were respectively synthesized by reaction of benzoic acid, acetic acid, and methanol with vinylbenzylchloride, then copolymerized with maleic anhydride. The measurements of the reactivity ratios of these three copolymerizations were carried out with a method using high conversions of the reactions. The results show a good correlation between a linear alternating structure for one of the copolymerizations were also performed with various percentages of initiator, giving similar proportions of incorporated monomers in the resulting products, and a relation between their viscosities and their weight molecular masses was presented. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1447–1454, 1999

Key words: maleic anhydride copolymers; reactivity ratios; molecular mass; viscosity

INTRODUCTION

The free radical copolymerizations between electron donor and electron acceptor monomers generally give alternating copolymers, and were widely studied when the electron acceptor was maleic anhydride or similar products such as maleimide.¹ It is well known that in usual conditions maleic anhydride cannot be homopolymerized, and only a few examples of polymerization are known.^{2,3} The copolymerization of styrene with maleic anhydride and its mechanism were studied both for academic and industrial demands.^{4,5} The classical schemes of the copolymerization, terminal, or penultimate model are generally inadequate, and the 1:1 charge-transfer complex in the propagation step provides a better understanding of the reaction. Only few examples of such copolymerizations were described with vinylbenzylchloride (VBC), a substituted styrene. The copolymerizations with maleic anhydride^{6,7} or with N-allyl maleimide⁸ also give alternating structures, and the reactivity ratios with maleic anhydride were measured.⁷ The alternating copolymers with maleic anhydride also have flame retardancy properties⁹ similar or sometimes better than those of poly vinylbenzylchloride. VBC is, in fact, a very versatile monomer due to the numerous nucleophilic substitutions reactions of the chlorine atom giving generally new monomers able to be polymerized.^{10,11} Various pyrazole groups were grafted onto VBC then polymerized

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Scheme 1 Synthesis route of substituted VBC 1a, b, c, and of substituted VBC-MAcopolymers.

or copolymerized with maleic anhydride to synthesize new chelating products.¹² In a previous work,⁹ a relation between the intrinsic viscosity of VBC-maleic anhydride copolymers and their molecular weights was established. To prepare new alternating copolymers of maleic anhydride and substituted styrenes, we have studied the copolymerization reaction of vinyl benzyl benzoate **1a**, vinyl benzyl acetate **1b**, and vinyl benzyl methyl ether **1c** with maleic anhydride. The measurements of the reactivity ratios of the copolymerizations with high yields, and the relations between the viscosities and molecular masses will be described.

EXPERIMENTAL

Apparatus and Measurements

VBC (a gift from Dow Chemical, France) was distilled under vacuum before use (50–55°C/0.5 mmHg). Maleic anhydride (MA) was twice recrystallized from chloroform and dried in vacuum for 24 h. The elemental analyses of the copolymers were performed at the Service Central d'Analyse (CNRS, Vernaison, France). The molecular masses of the copolymers were measured with a Knauer apparatus by using $10^3 - 10^5$ Å columns, polystyrene standards, and tetrahydrofuran (THF) as solvent. The viscosity measurements were carried out in a Schott-Gerate AVS automated viscosity measuring system in dimethylformamide (DMF) at 25°C using an Ubbelhode type viscometer with low shear rate. The temperature was controlled to within 0.01°C and the error of the flow times was 0.01%. The viscosity data were extrapolated to zero concentration to obtain values for intrinsic viscosity $[\eta]$ according to the Huggins equation $\eta_{\rm sp}/c$ = [η] + $k'[\eta]^2 c$, where c is the polymer concentration, $\eta_{\rm sp}/c$ is the reduced viscosity, and k' is the Huggins constant. IR spectra of copolymers were recorded with a Bio-Rad FT S-7 apparatus. Copolymers were characterized by ¹³C-NMR: the spectra were recorded with a Bruker AC 200 spectrometer at 50.3 MHz with a 50% solution in deuterated dimethyl sulfoxide CD₃SOCD₃ with tetramethyl silane as an internal reference.

Monomers 1a, b, and c

The three substituted styrenes were prepared by nucleophilic substitutions of the chlorine atom of VBC with the corresponding nucleophile. Substituted VBC **1a** was synthesized by using previously described procedures with benzoic acid as the reactant, dimethyl formamide as the solvent, and triethylamine as the catalyst.¹³ The acetate **1b** was prepared by reaction of acetic acid or potassium acetate according to two known methods.^{14,15} The ether **1c** was obtained from the reaction of methanol with sodium hydroxide.¹⁶

Copolymers 2 a, b, and c

Copolymer **2a** (X = C_6H_5CO) was prepared by heating a mixture of **1a** and MA with azobis isobutyronitrile (AIBN) as initiator in a solution of toluene after degassing of the tube. A typical run is described for an equimolar proportions of **1a** and MA: 0.7 g of **1a** and 0.288 g of MA with 2 mg of AIBN are dissolved in 5 mL toluene. After degassing, the tube was sealed and heated for 48 h at 75°C, then the content of the tube was precipitated by methanol then twice dissolved in chloroform and precipitated by methanol. The yields are generally in the range 60–90% (massic yields). Similar procedures were used for the preparations of copolymers **2b** and **2c**, but acetonitrile was used as the solvent instead of toluene, because the copolymerization, in this solvent, only provides insoluble products. The copolymers used for determination of $[\eta] - \overline{M}_w$ relations were obtained in solution (acetonitrile) with various molar concentrations of AIBN. These copolymers were purified by several washing with methanol/ acetone (90/10, v/v) for extraction of low molecular masses products. According to their IR spectra, similar to those of the copolymers, the low molecular masses products have probably the same chemical structure.

RESULTS AND DISCUSSION

Structures of the Copolymers and Measurement of the Reactivity Ratios

The structures of the copolymers were first studied by IR Spectroscopy: the IR spectra of the three products show peaks at 1850 and 1780 cm⁻¹ due to the anhydride group. The carbonyl absorptions of 2a (benzoate) and of 2b (acetate) were, respectively, observed at 1715 and 1735 cm^{-1} , and there is no peak between 3600 and 3000 cm^{-1} , which could be attributed to the carboxyl group of maleic acid.The ¹³C-NMR spectra were recorded with samples prepared with various proportions of the starting monomers (1a, 1b, or 1c) with MA. But, due to the insolubility of the copolymers in almost all the organic solvents, the spectra were recorded in deuterated dimethylsulfoxide (DMSO d_6) and, unfortunately, some peaks attributed to the C_{α} and C_{β} carbons of the styrene units and to the C_{α} and $\mathbf{C}_{\alpha}^{''}$ carbons of the MA units are overlapped by the solvent. The chemical shifts of similar products were previously described: in the four methoxystyrene-maleic anhydride or in the styrene-maleic copolymers, the chemical shifts of C_a and C_{β} are, respectively, 52 and 43 ppm, and for C_{α}' and C_{α}'' similar values were observed.^{17,18} The ¹³C-NMR were also studied by comparison with those of numerous substituted polystyrenes.¹⁹ Specific peaks can be attributed to the methylene group in (2a, 2b, and 2c), respectively, at 65 ppm for the CH_2 —OCOR (R = phenyl **2a** or $R = methyl \ 2b)$ or at 74.1 ppm for \underline{CH}_2 —OCH₃ (2c). The methyl group of the acetyl group (2b) and of the methoxy group (2c) are respectively located at 20.5 and 58 ppm (Table I). The comparison of areas of peaks due to the CO (copolymer 2a), to the CH₃ and to the carbonyls (copolymer 2b), to the CH₂ and to the carbonyls of MA (copolymer **2c**) shows that the proportions of styrenes and of MA are in the range of 45–55%, and in good correlation with the results of the elemental analyses (Table II). As a full understanding of the structure of the copolymers, probably alternating, is difficult, the diagrams of composition were necessary. The results are given in the Table III with the corresponding molecular masses and the diagrams in Figure 1. The variations of the copolymer composition compared to the molar fraction of the styrenic monomers show that the three copolymers have a strong tendancy to alternancy, but the products **2b** and **2c** are probably partially crosslinked: the measurements of their molecular masses (Table III) give high polydispersity indexes, and in some experiences the results were not coherent due to the partial solubility of the copolymer. The crosslinking reaction or the transfer reaction to the copolymer is probably due to the methyl group of the acetate function (copolymer **2b**) or of the ether function (copolymer **2c**).

	2a	2b	2c	
$C_{\alpha}, C_{\beta}, C_{\alpha}', C_{\alpha}''$	Nonvisible	Nonvisible	Nonvisible	
OCOCH ₃		20.5		
OCH_3			58	
$CH_2 - OCOCH_3$	65	65.2		
$\overline{\mathrm{CH}_2}$ —OCH ₃			74.1	
$\overline{C_1 - C_6}$	124 - 138	125 - 143	125 - 143	
$C'_1 - C'_4$	124–138			
$-CH_2-CO$	165.5	170		
<u>CO</u> (MA)	173.2	173.2	173.2	

Table I Chemical Shifts in ¹³C-NMR (δ ppm) of the Copolymers 2a, b, and c

		Percentages of Incorporated Monomers		
Initial Molar Proportion of Monomers	0%	a mol/mol	ь mol/mol	
$\frac{1a}{MA} = \frac{50}{50}$	23.31	51.7/48.3	49.3/50.7	
$\frac{1b}{MA} = \frac{60}{40}$	29.17	50.1/49.9	54/46	
$\frac{1}{MA} = \frac{45.7}{50.3}$	25.74	50.7/49.3	50.5/49.5	

Table II	Elemental A	Analyses of	f Oxygen	in the	Copolymer	2a, b, c	, and
Percenta	ges of Incor	porated in	the Cope	olymer	5		

^a Calculated by elemental analysis of oxygen. ^b Calculated by measurement of areas in ¹³C-NMR.

In spite of these drawbacks, the experimental measurements of the reactivity ratios were performed by using the values of molar fractions of monomers in the copolymers (Table III). These results were obtained with generally high conversions of the reactions, and it is known that the

main methods (Fineman-Ross²⁰ or Kelen-Tudös²¹) need low conversions of the reaction or less than 30% of conversion for the Kelen-Tudös method. Recent works describe new methods to obtain the values of reactivity ratios with high yields of copolymerization, in the penultimate

Table III Copolymers Composition, Massic Conversions,^a Molecular Weights (\overline{M}_n and \overline{M}_w), Polydispersity Indexes (f_1 , Molar Fraction of 1a, or 1b or 1c in the Feed and F_1 , Molar Fraction of 1a, or 1b or 1c in the Copolymer)

	f_1	F_1	$\begin{array}{c} \text{Conversion} \\ \% \end{array}$	${ar M_n} {10^{-5}}$	${ar M}_w$ 10 $^{-5}$	I
Copolymer 2a	0.1	0.48	21	1.71	4.42	2.58
1 0	0.2	0.44	75	0.73	3.26	4.46
	0.3	0.45	71	1.88	4.06	2.15
	0.4	0.47	65	1.83	4.43	2.42
	0.5	0.51	91	1.99	4.44	2.23
	0.8	0.77	95.8	0.18	0.93	5.16
	0.9	0.89	95.6	0.3	0.8	2.67
Copolymer 2b	0.2	0.5	50	Insoluble	Insoluble	
1 V	0.3	0.4	51	0.25	2.08	8.32
	0.5	0.43	94	0.84	2.2	2.6
	0.6	0.5	75	0.53	1.9	3.58
	0.7	0.58	61	0.44	1.43	2.67
	0.78	0.66	54.3	Insoluble	Insoluble	
Copolymer 2c	0.3	0.44	66	0.33	1.84	5.6
	0.5	0.5	67	0.4	1.62	4.05
	0.6	0.55	83.3	0.14	0.95	6.78
	0.7	0.56	62	0.39	1.76	4.51
	0.8	0.62	38	0.43	1.37	3.18
	0.9	0.72	65	0.07	0.21	3

^a The calculations of reactivity ratios were carried out with massic conversions inferior to 85%.



Figure 1 Composition diagrams of copolymers 2a, 2b, and 2c.

model²² when one of the reactivity ratio is equal to zero and in the terminal model.²³ The method of R. B. Mao and M. B. Huglin was used with some experimental data given in Table III and with conversions lower than 85%. It is clear that conversions of 90-95% implies that all the monomers were copolymerized, and the composition of the copolymer is practically the same as for the monomer mixture. In spite of the side reactions the main structure of copolymers **2b** and **2c** may be considered as alternating. These data were used for the composition curves given in Figure 1. The calculation uses a linear least-squares method involving several iterations, and the basis of the work is the classical differential copolymerization equation and the Kelen-Tudös method. A linear method of calculation of reactivity ratios is used for copolymerizations up to very high conversions. The basic principle and the iterative procedure for calculating reactivity ratios by using any high conversion data of the terminal model have been described.^{22,23} The method applied in this procedure at high conversion necessitates several iterations, and the calculation is based on the differential copolymerization equation.

The principle of calculations are the following: for a series of experimental data points $f_0(i)$, F^e (i), θ (i), i = 1, 2, ..., n, the reactivity ratios are calculated by the following iterations steps: (1)initial values $r_1^{(0)}$, $r_2^{(0)}$ are assigned; (2) their validities are tested by: (a) using $r_1^{(0)}, r_2^{(0)}, f_0(i)$, and the conversion $\theta(i)$ to calculate $F^{c(0)}(i), f_0(i)$ is the ratio of mole fractions of two monomers in the initial feed. $F^{c(0)}(i)$, the copolymer composition, is obtained by integrating the differential equation of composition numerically step by step. The process is repeated to the given conversion θ for that experimental point (i). This method needs a computer program (the authors thank Dr. R. Mao for his help and for sending the computer program). The number of iterations for the calculation of the reactivity ratios was 14. (b) using $F^{c(0)}(i)$ in conjunction with equation:

$$f^{c}(i) = rac{[F^{c}(i)-1] + \sqrt{[1-F^{c}(i)]^{2} + 4r_{1}r_{2}F^{c}(i)}}{2r_{1}}$$

to calculate: $f^{c(0)}(i)$.

 f^c : calculated instantaneous monomer feed at t = t. The methods of Kelen-Tudös and Fineman-Ross used the initial monomer feed composition f_0 . In the procedure used to very high conversion, f_0 is replaced by f^c , and the Kelen-Tudös method is applied. (c) f^c (0) (i), F^e (i), are used, and the

Copolymerization	r_1	r_2	$r_1 imes r_2$
1a/MA	0.09	0.04	0.04
1b /MA	0.10	0.11	0.01
1c/MA	0.10	0.23	0.02

Table IV Reactivities Ratios r_1 and r_2 of the **Copolymerization Reactions** of 1a, b, and c with MA

Kelen-Tudös plot method is adopted to obtain new

values of the reactivity ratios $r_1^{(1)}$, $r_2^{(2)}$. If $r_1^{(1)} \neq r_1^{(0)}$ or $r_2^{(1)} \neq r_2^{(0)}$, $r_1^{(1)}$, $r_2^{(1)}$ are tested by a similar procedure.

The iteration steps are repeated until:

$$|r_1^{(k)} - r_1^{(k-1)}| < arepsilon ext{ and } |r_2^{(k)} - r_2^{(k-1)}| < arepsilon$$

where ε is a very small value.

If the difference between two consecutive calculated reactivity ratios is smaller than ε , then the reactivity ratio may be considered to have attained constant values. The application of this method with the experimental data of the Table III provides the following results for the three copolymerizations (r_2 is attributed to MA and r_1 to the styrenic monomer **1a**, **b**, or **c**). The values of r_1 are close to 0.1, but the values of r_2 are in the range 0.04–0.23 (Table IV). The tendancy to alternancy is thus demonstrated but the reactivity ratios of MA for the two copolymerization reactions vinylbenzylacetate-(1b)- and vinylbenzylether (1c)-MA are too strong and quite different from those generally reported in the literature.²⁴ The used method for the calculation of the reactivity ratios is based on the values of the conversions and on the theory of the terminal model. The two copolymerization reactions provide partially insoluble products due to a transfer reaction giving crosslinked copolymers and, therefore, the value of yields are different from those obtained in copolymerization reaction without branching. Also, it must be noticed that the vinyl benzyl chloride is a mixture of *meta* and para isomers, the reactivities of which are identical, and no anomalous effect was observed even with a bulky substituant such as a benzoate group.

Relations between Viscosities and Molecular Weights

To obtain a relation between viscosity and weight-average molecular masses, several copolymerizations with equimolar proportions of substituted styrenes and maleic anhydride were carried out and the percentage of initiator varied for each essay (Table V).

Plots of ln $[\eta]$ vs. ln $\overline{M_w}$ in DMF are shown in Figure 2 for the copolymers $2a_{1-5}$, $2b_{1-5}$, and $2c_{1-5}$ (Table V). The following equations ([η] in ml/g) at 25°C were obtained:

Table V Molecular Weights and Viscosities for Copolymers 2a₁₋₅, 2b₁₋₅, and 2c₁₋₅

Copolymer	[η] mL/g	$ar{M}_w$ 10 $^{-$ 3	$ar{M}_n$ 10 $^{-$ 3	$\mathbf{I} = \bar{M}_w / \bar{M}_n$	Concentration of AIBN 10 ⁻² mol/L
2a.	39.80	217	98	2.2	0.1
$2a_{2}$	36.30	173	60	2.9	0.3
$2a_3$	30.30	150	28	5.4	0.6
$2a_{A}$	27.00	130	39	3.3	3
$2a_5$	19.00	87	36	2.4	6
$2\mathbf{b}_1$	39.60	278	99	2.8	0.1
$\mathbf{2b}_{2}$	38.20	220	84	2.6	0.3
$2\mathbf{b}_{3}$	28.20	138	51	2.7	0.6
$\mathbf{2b}_{4}$	18.50	77	31	2.5	3
$\mathbf{2b}_{5}$	15.00	68	29	2.3	6
$2c_1$	29.0	166	57	2.9	0.1
$2c_2$	28.70	132	43	3.1	0.3
$2\mathbf{c}_{3}$	24.60	110	41	2.7	0.6
$2c_4$	17.10	74	34	2.2	3
$2c_5$	14.70	55	33	1.66	6



Figure 2 Relations between viscosities and molecular weights for copolymers **2a**, **2b**, and **2c** in DMF at 24°C.

$$[\eta] = 1.68 \cdot 10^{-3} M_w^{0.822} (\mathbf{2a})$$
$$[\eta] = 7.84 \cdot 10^{-3} M_w^{0.687} (\mathbf{2b})$$
$$[\eta] = 8.26 \cdot 10^{-3} M_w^{0.685} (\mathbf{2c})$$

These relations were also verified for the copolymer with equimolar composition but obtained by using various initial molar fractions of the comonomers. As previously discussed, the composition curves of the three copolymers show, for equimolar composition of the starting feed, that the percentages of incorporated monomers are close to a ratio 1/1. The value of the constant a = 0.82 from Kuhn-Mark-Houwink-Sakurada equation shows a higher rigidity of the molecular coils for the **2a** copolymer than for the other copolymers **2b** and **2c**. This rigidity is probably due to the volume of benzoate substituent.

Propagation Mode of the Reaction

Free radical copolymerization reactions between styrene and maleic anhydride¹ or N-substituted maleimide were reported in many articles,^{25,26} and numerous studies deal with the propagation mode of the reaction, which can be explained by a terminal, penultimate, or complex model. The calculation of a reactivity ratio when the other reactivity ratio is equal to zero is relatively easy in a penultimate model. As the method of R. W. Mao et al. can be used in this case,²² an attempt to determinate the values of the two ratios r_1 and r_1 was carried out in the copolymerization of monomer 1a with MA. This reaction was chosen due to the lack of a crosslinking reaction, but the calculated values are anomalous, and do not allow for proposition of a penultimate model. Recent works have studied the copolymerization reactions of N-phenylmaleimide with styrene^{27,28} and of maleic anhydride with four chlorostyrene.²⁹ The kinetic studies showed that both the charge-transfer complex and free monomers participate in the copolymerization process, and therefore, further works will be necessary to verify this hypothesis in the three substituted styrenes-maleic anhydride copolymerization reactions.

CONCLUSION

The copolymerization of MA with styrenes substituted with bulky or not bulky substituents provide copolymers rich in alternating structures. The determination of reactivity ratios, calculated with a recent method using high conversions of the copolymerization confirms this hypothesis. But, despite composition curves in agreement with alternating structures, the obtained values of reactivity ratios with two other copolymers are too high for MA. Theses anomalous results are probably due to a transfer reaction with partial crosslinking.

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