On the reactivity of aromatic acrylates in free-radical copolymerization with SO_2 and terpolymerization with SO_2 and 1-heptene

Zbigniew Florjańczyk and Ewa Zygadło
Institute of Polymer Technology, Technical University (Politechnika), ul Noakowskiego 3, 00-664 Warsaw, Poland

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The free-radical copolymerization of SO_2 with phenyl, *p*-t-butylphenyl, *p*-nitrophenyl and 1-naphthyl acrylates and the terpolymerization of those monomers with 1-heptene were studied. The maximum content of sulphonyl monomeric units in copolymers varies from 13 to 24% depending on the induction and steric effects of the acrylic substituents. The composition of terpolymers varies over a very wide range depending on the reactant mole ratio and conversion. The composition of both copolymers and terpolymers is only affected to a small extent by temperature, contrary to the analogous reactions with alkyl acrylates.

(Keywords: sulphur dioxide copolymers and terpolymers; phenyl acrylate; *p*-nitrophenyl acrylate; *p*-t-butylphenyl acrylate; 1-naphthyl acrylate; 1-heptene)

INTRODUCTION

It was found previously in our laboratory that sulphur dioxide undergoes free-radical copolymerization with alkyl acrylates[1]. ^{13}C n.m.r. spectra indicate that acrylic monomeric units (m.u.) occur in these copolymers as homosequences of various length, separated by individual SO_2 m.u. The minimum length of acrylic (A) homosequences is 2 m.u. This means that stable incorporation of SO_2 into the growing chain is possible only when an AA diad occurs at the chain end.

Analysis of the kinetic model indicates that SO_2 addition is strongly reversible even at $-78°C$ (ref. 2) and the addition of all acrylates to the growing chain is practically irreversible. The composition of the copolymers obtained and sequence distribution practically do not depend on the kind of alkyl substituent in the ester group[1].

In this paper we report the first examples of copolymerization and terpolymerization in systems comprising SO_2 and acrylates with aromatic substituents in the ester group (phenyl, *p*-t-butylphenyl, *p*-nitrophenyl and 1-naphthyl). The main goal of these studies was to estimate the influence of the kind of substituent on the ease of SO_2 incorporation into the growing chain.

RESULTS AND DISCUSSION

Copolymerization

The copolymerization of SO_2 with aromatic acrylates or methyl acrylate was carried out in bulk in the presence of t-butyl hydroperoxide or azobisisobutyronitrile (AIBN) as initiator within the -78 to 50°C temperature range. The results of these reactions are presented in *Table 1*. The maximum SO_2 content in copolymers with aromatic esters varies from ≈ 13 to ≈ 24 mol% (the use of a larger excess of SO_2 did not cause essential changes in the copolymer compositions, but led to a remarkable decrease in the reaction rate). It is lower at $-78°C$ than in the products of analogous reactions with methyl acrylate, but at $+50°C$ it is considerably higher. The influence of temperature on the copolymer composition in reactions with aromatic acrylates is very small, contrary to the copolymerization of SO_2 with alkyl acrylates[1], styrene[3], vinyl chloride[4] and other monomers, which do not form strictly alternating copolymers with SO_2.

As was shown previously[2], the SO_2 copolymerization with alkyl acrylates can be described by the following kinetic model:

$$\sim AA^{\cdot} + SO_2 \underset{k_{dAASO_2}}{\overset{k_{AASO_2}}{\rightleftharpoons}} \sim AASO_2^{\cdot} \qquad (1)$$

$$\sim ASO_2^{\cdot} + A \xrightarrow{k_{ASO_2A}} \sim ASO_2A^{\cdot} \qquad (2)$$

$$\sim SO_2A^{\cdot} + A \xrightarrow{k_{SO_2A}} \sim SO_2AA^{\cdot} \qquad (3)$$

$$\sim AA^{\cdot} + A \xrightarrow{k_{AAA}} \sim AAA^{\cdot} \qquad (4)$$

The expression for the copolymer composition contains two reactivity ratios, $r_{AA} = k_{AAA}/k_{AASO_2}$ and $r'_{ASO_2} = k_{dAASO_2}/k_{ASO_2A}$. Assuming the same model for the results now obtained, one can expect that in reactions with aromatic acrylates r'_{ASO_2}, i.e. the ratio of $\sim AASO_2^{\cdot}$ macroradical depropagation rate constant to the rate constant of acrylate addition to that radical (reaction (2)), changes only slightly with a temperature rise. In systems known hitherto, the depropagation rate constants increased much quicker than those of propagation. The intramolecular interaction between the singly occupied molecular orbital (SOMO) of the macroradical and frontier orbitals of the aromatic ring probably leads to a greater stabilization of the system.

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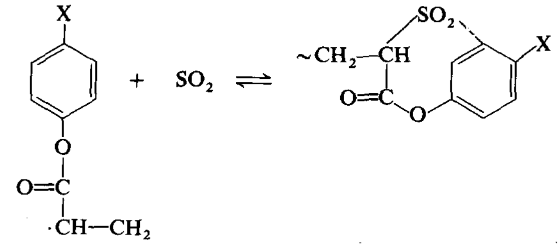

(5)

Table 1 Copolymerization of sulphur dioxide with various acrylates[a]

Acrylate	Temp. (°C)	Reaction time (min)	Acrylate conversion (%)	SO_2 m.u. content in copolymer (mol%)
Methyl	−78	1	4.5	30
	0	60	7.1	13
	50[b]	30	27.6	4
Phenyl	−78	120	18.4	18
	50[b]	180	6.9	15
p-t-Butylphenyl	−78	120	7.8	24
	0	300	14.3	20
	50[b]	60	13.0	15
		180	66.4	15
p-Nitrophenyl	−78	20	16.6	12
		120	81.6	13
	[c]	60	34.7	10
	[d]	180	52.3	12
	0	180	11.5	12
	50[b]	15	15.5	14
1-Naphthyl	−78	30	16.4	11
		60	27.9	14
	0	60	7.3	14
	50[b]	90	30.9	13

[a] SO_2 mass = 10 g; initiator: t-butyl hydroperoxide, 1 wt% with respect to SO_2; SO_2/acrylate mole ratio in monomer feed = 1:30
[b] Initiator: AIBN, 1 wt% with respect to SO_2
[c] Acrylate/SO_2 mole ratio = 1:20
[d] Acrylate/SO_2 mole ratio = 1:100

Thus, the composition of copolymers obtained at −78°C indicates that the relative reactivity ratios for aromatic acrylates are higher than those for aliphatic acrylates. The higher resonance stabilization of aromatic esters is probably the reason for this. The lower content of SO_2 m.u. in copolymers with 1-naphthyl acrylate than that in copolymers with phenyl acrylate can also be explained by that effect. However, it cannot be excluded that the difference in reactivity results also from steric effects. It is quite clear that in the case of phenyl derivatives the ease of SO_2 addition into the growing chain depends on the induction effect of the substituent in the aromatic ring. The NO_2 group, abstracting electrons, hinders SO_2 addition; and the t-butyl group, with a positive induction effect, facilitates the addition of the monomer. This is understandable since SO_2 is characterized by strong electrophilic properties and the size of the partial positive charge on the carbon atom, with which it forms a bond, probably has an essential effect on the rates of both propagation and depropagation. Despite the fact that the effect of the substituent at the *para* position in aromatic esters is transmitted through many bonds, it is known to have a remarkable influence on the value of the *e* parameter of the monomer[5].

Terpolymerization

The mole ratio of acrylic m.u. to SO_2 m.u. in aliphatic polysulphones may vary over a wide range, provided that an electron-donor monomer is additionally introduced into the polymerization system[6]. In *Table 2* are presented the compositions of some terpolymers of SO_2, aromatic acrylates and 1-heptene obtained in systems containing a large excess of SO_2 with respect to the other monomers. At an equimolar amount of acrylate and 1-heptene in the monomer feed and conversion up to ~50%, products are obtained in these reactions containing mainly SO_2 and electron-donor m.u., and the acrylic m.u. content

Table 2 Terpolymerization of sulphur dioxide and 1-heptene (D) with aromatic acrylates (A)[a]

Acrylate	Monomer mole ratio			Temp. (°C)	Acrylate conversion (%)	m.u. content in terpolymer		
	SO_2	A	D			SO_2	A	D
Phenyl	30	1	1	−78	3.3	44	12	44
	300	10	1		17.7	42	21	37
p-t-Butylphenyl	30	1	1	−78	0.4	51	2	47
	30	2	1		6.6	49	3	48
	300	10	1		9.0	10	86	4
p-Nitrophenyl	30	1	1	−78	15.1	48	7	45
				20	12.7	47	9	44
	300	10	1	−78	28.1			
					8.5[b]	15	73	11
					19.6[c]	30	44	26
				20	61.8			
					31.7[b]	17	77	6
					30.1[c]	19	64	17
1-Naphthyl	30	1	1	−78	13.7	50	9	41
				20	11.4	44	11	45
	300	10	1	−78	1.6	26	48	26

[a] SO_2 mass = 30 g; initiator: t-butyl hydroperoxide, 1 wt% with respect to SO_2; reaction time 1–15 min
[b] Fraction insoluble in acetone
[c] Fraction soluble in acetone

varies from 2 to 12 mol%. *p*-t-Butylphenyl acrylate undergoes incorporation into the chain with the greatest difficulty, but the relative reactivities of the remaining acrylates are similar to one another. The use of considerable excess of an acrylate with respect to 1-heptene causes in many cases the acrylic m.u. to be the main component of the product. The terpolymer composition is in this case very heterogeneous. As can be seen for the terpolymer of *p*-nitrophenyl acrylate, at ten-fold excess of acrylate towards 1-heptene and conversion of 23.1%, fractions occur in which the difference in the acrylic m.u. content is ca. 30 mol%. The content of acrylic m.u. somewhat increases with a rise of temperature, and that of SO_2 m.u. decreases.

It is known that the rate of SO_2 addition to macroradicals with nucleophilic properties is a few orders of magnitude higher than the rate constant of vinyl monomer addition to these macroradicals[7]. Therefore, at an excess of SO_2 in the monomer feed it can be assumed that SO_2 undergoes selective addition to macroradicals terminated by 1-heptene (D) m.u.:

$$\sim D^{\cdot} + SO_2 \rightleftharpoons \sim DSO_2^{\cdot} \qquad (6)$$

Both an electron-donor monomer and acrylate undergo addition to macroradicals terminated by SO_2 m.u.:

$$\sim SO_2^{\cdot} + D \rightleftharpoons \sim SO_2D^{\cdot} \qquad (7)$$

$$\sim SO_2^{\cdot} + A \rightleftharpoons \sim SO_2A^{\cdot} \qquad (8)$$

The addition of electron-donor monomer is favoured in the case of an equimolar amount of it and the acrylate. This results from the strongly electrophilic character of a macroradical terminated by a SO_2 m.u., and the interactions between SOMO of the radical and highest occupied molecular orbital (HOMO) of the monomer may decide to a greater extent the activation energy in the propagation step than the SOMO–LUMO (lowest unoccupied molecular orbital) interactions.

All monomers can theoretically add to macroradicals terminated with an acrylic m.u.:

$$\sim A^{\cdot} + SO_2 \rightleftharpoons \sim ASO_2^{\cdot} \qquad (9)$$

$$\sim A^{\cdot} + A \rightleftharpoons \sim AA^{\cdot} \qquad (10)$$

$$\sim A^{\cdot} + D \rightleftharpoons \sim AD^{\cdot} \qquad (11)$$

As can be seen from *Table 2*, in some systems the SO_2 m.u. content is nearly 50 mol%. This indicates that reaction (9) occurs much faster than reaction (11) and short homosequences of A are terminated from both sides by SO_2 m.u.

It can be suggested that in terpolymers containing a similar amount of SO_2 and 1-heptene m.u. the acrylic m.u. homosequence termination proceeds mainly as a result of the electron-donor monomer addition (equation (11)), since these homosequences start from the acrylate addition to SO_2 m.u. (equation (8)). However, the accuracy of terpolymer composition determinations (ca. ±1% for each kind of m.u.) is not adequate to formulate conclusions on the effect of the structure of reactants on the proportion of competitive reactions (9) and (11). It can only be suggested on the basis of studies on the copolymerization of alkyl acrylates with SO_2[1,2] and olefins[8] that the rate constants of these reactions are considerably lower than that of the acrylate homopropagation (reaction (10)). It cannot be excluded that both SO_2 and 1-heptene incorporate into the growing chain as a result of interactions between the macroradicals and charge-transfer complex between these monomers.

The copolymers and terpolymers of *p*-nitrophenyl, *p*-t-butylphenyl and naphthyl acrylates obtained in this work exhibit strong absorption bands in u.v. spectra at 267, 275 and 281 nm, respectively. At present studies are being carried out on the photodegradation of these polymers and their applicability as positive resists.

EXPERIMENTAL

Phenyl, naphthyl, *p*-t-butylphenyl and *p*-nitrophenyl acrylates were obtained from the reaction of acryloyl chloride with corresponding phenols and purified by vacuum distillation. The structure of all the monomers was confirmed by elemental analysis and i.r. and ^1H n.m.r. spectroscopy. The methods of purification of reactants and of the polymerizations have already been described in detail[1,6]. The polymerizations were terminated by adding a large amount of methanol. The products isolated were dried to constant weight at 40°C, and their composition was determined by elemental analysis. U.v. spectra were recorded in acetonitrile solutions.

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