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Synthesis and characterization of some polymers with applications in non-linear optics II. Copolymerization of styrene with some monomers containing azo-dyes

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Abstract

The present work describes the evolution of binary copolymerization of a monomer containing an azoic chromophore with styrene. Reactivity ratios have been computed using several methods. The sequential analysis suggests a favourable case for the use of azoic structures in electro-optical applications.

1. Introduction

Construction of a macromolecular structure with a predictable architecture which is useful for non-linear optical (NLO) applications is often performed through copolymerization of conventional monomers (styrene (S), methyl methacrylate (MMA)) with co-monomers (CM), which have chromophore fragments incorporated in their composition. In this case, the main restriction to be satisfied consists of the fact that the structure of CM (or its degree of purity) should not hinder the copolymerization process, for instance CM should not participate in intensive chain transfer reactions, thus limiting the molecular weight. In previous works, we have reported the preparation and use in copolymerization of such CMs [1,2]. The data obtained have given evidence for the following primary information:

- Coloured monomers (CM) may be chemically incorporated in a glassy matrix of PS or PMMA; however, the maximum concentration of CM is decided by their intense chain transfer activity, and consequently the polymerization degree is drastically limited to unsuitable values for practical applications. Even in small concentrations, CM produces a certain increase in overall polymerization rate.
- In the copolymer chain, the repeat units from CM maintain the optical properties characteristic to the initial monomers.

2. Experimental

Among CMs synthesized, the most interesting one (from the point of view of electro-optical properties of the copolymer) is the following azoic monomer with a styrenic skeleton (**B4**):

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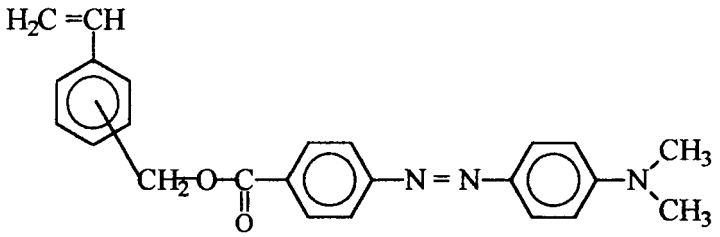

To obtain the reactivity ratios for the pair S–**B4**, several copolymerization tests were performed; the molar fraction of CM (x_2) in the initial monomer feed was kept in the range 0.1–0.8. Polymerization was carried out at 80°C, initiated by azo-iso-butyro-dinytrile (AIBN) in concentrated homogeneous solution (chloro-benzene—CB), or even in bulk, using the dilatometric technique (for monomer feeds rich in S), or in vials (monomer feeds containing more **B4**); all experiments were carried out in an oxygen-free atmosphere (argon). Kinetic data have been previously reported [2]. Polymer separation from the reaction mixture was accomplished by a rough precipitation in methanol (M), followed by dissolution (CB)/re-precipitation (M)/filtration cycles, to the complete disappearance of the colour in the filtrate.

The average molar masses of the copolymers synthesized were obtained through gel permeation chromatography (Waters, 25°C, THF as solvent); the values for M_n are within the limits inherent in the Mayo–Lewis equation. The molar fractions of CM units in copolymer were calculated based on ^{1}H-NMR spectra (apparatus-Bruker WP 300, $CDCl_3$ as solvent, standard-TMS as well as on elemental analyses.

3. Results and discussion

Table 1 reveals the copolymerization tests performed for the pair S–**B4**. As may be seen from the table, CM may be incorporated in a copolymer chain up to a satisfactory level; a quick comparison of values for the pairs x_2 and X_2 suggests (despite rather different final conversions) a behaviour close to the ideal one. As the final conversions were lower than 30%, the reactivity ratios were estimated by using differential methods such as Kelen–Tudos, (KT) Mayo–Lewis (ML), Fineman–Ross (FR), or Yezrielev–Brohina-Roskin (YBR); the results are presented in Table 2 [3]. More precise results may be obtained with the Tidwell–Mortimer (TM) method [4]; the mathematical treatment is essentially non-linear. Hagiopol and coworkers [5] have proposed other non-linear methods (OPT-2, OPT-2C) for calculating reactivity ratios. The OPT-2

Table 1
Copolymerization of the pair S–**B4** in CB at 80°C

10^2 **B4** (mol/l)	C (%)	$10^3 x_1^{*a}$	$10^3 X_1^*$	$10^3 M_n$
0.00	6.24	0.0	0.0	67.50
1.08	5.25	2.7	2.5	55.10
2.16	6.11	5.4	4.7	50.40
3.24	6.13	8.0	8.6	38.00
4.42	5.95	11.0	10.7	29.60
5.40	5.62	13.3	13.0	20.20
6.48	5.76	16.0	14.0	19.50
0.43	50.00	150.00	147.0	110.00
0.50	25.00	480.0	470.0	–
0.75	24.50	722.0	717.0	–
0.80	27.00	780.0	670.0	–

[a] x^*, X^* = CM molar fractions in monomer feed and in copolymer, respectively.

Table 2
Relative reactivity ratios obtained by using various calculation methods

Method	r_1	r_2
FR1	0.51	0.91
FR2	2.33	1.08
KT	0.82	1.06
YBR	0.66	1.06
TM	0.64	0.82
OPT-2C	0.58	0.77

method uses the classical Mayo–Lewis equation in its differential form, so it may be applied only for low conversions; OPT-2C, may be used regardless of conversion as it takes advantage of numerical integration of the composition equation.

Table 2 presents the values obtained using classical linear methods (FR, YBR, KT), as well as non-linear methods (TM, OPT-2, OPT-2C). Analysing the data presented in Table 2, it seems that the best estimates are given by the OPT-2C method; the same is obvious from the 95% confidence domain, as shown in Fig. 1. Both OPT-2C and TM are close, from the point of view of precision, unlike other methods (see Table 2 and Fig. 1); although the FR method is still frequently used, it shows a lower accuracy (see the huge difference arising when re-indexing the monomers—FR2).

Since monomer **B4** has a bulky substituent, we have checked the penultimate model for the system S–**B4**, trying to calculate the corresponding parameters. Calculations performed with the method OPT-4C [6] have led to the results: $r_{11} = 0.22$; $r_{22} = 2.75$; $r_{21} = 1.5 \times 10^4$; $r_{12} = 0.47$. To decide which model is the actual one, we have performed a discriminating statistical test ($F^s_c(2.6)$) [7].

It may be shown that the condition for the penultimate model being effective within a 95% probability implies the value $F^s_c(2.6) \geq 5.14$; as the actual value obtained is only $F^s_c = 1.55$ it may be said that the system obeys the rules of the ultimate model.

Based on the most precise values for reactivity ratios, we have estimated the 'Q and e' parameters, as well as the sequential distribution of the repeat units in copolymer; we have obtained $Q = 0.36$ and $e = 1.2$ (the azoic chromophore reduces the radical reactivity).

The distribution of **B4** repeat units seem to be a favourable one, as for values $X_{B4} < 0.2$ (convenient for further applications) the chromophores are distributed one by one in the continuous matrix of PS.

4. Conclusions

- We have performed the copolymerization of S with an azoic monomer synthesized and characterized by us; such copolymers are useful in non-linear optics.
- Several analytical methods have been used in order to compute the reactivity ratios; the best results were obtained by using the OPT-2C method.
- The values obtained for parameters 'Q and e' for monomer **B4** are in agreement with the structure of this monomer.
- The sequential distribution, calculated based on reactivity ratios, is favourable for applications in non-linear optics.

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