Radical copolymerization of styrene and acrylonitrile in the presence of oligooxyethylene azoester

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Abstract: Telechelic vinyl oligomers terminated with hydroxyl groups were prepared by free radical copolymerization of styrene (S) and acrylonitrile (AN), initiated by azoester–2,2'-azobis[2-methyl-ω-hydroxy-oligo(oxyethylene) propionate] [AIB-OOE(400)], carried out in *N,N*-dimethylformamide. The reactivity ratios r_S=0,225 and r_{AN}=0,722 for styrene and acrylonitrile, respectively, were evaluated by Kelen–Tüdős method. The glass transition temperatures (T_g) of the copolymers were determined by differential scanning calorimetry. T_g values varied with the copolymer composition in the range of 60-82 °C and the maximum T_g value was obtained for copolymer with 60 mol% AN.

Introduction

The process of radical copolymerization of styrene and acrylonitrile has been the subject of many investigations [1-9]. The copolymerizations were carried out at different environments, and the kinetics and mechanism of polyreactions, as well as the structure and properties of obtained copolymers have been studied [1-3]. The investigators view relating to the mechanism of styrene (S) – acrylonitrile (AN) copolymerization is divided on this issue. Some of them claim that this copolymerization is a marked example of the occurrence of penultimate unit effect [4, 5], the others claim that the terminal model also adequately describes the reaction mechanism [6-8]. Determined reactivity ratios of the comonomers ranged from 0.04 to 0.34 for acrylonitrile and from 0.14 to 0.54 for styrene [10]. They are differentiated depending on the reaction conditions and methods of their evaluation. The SAN copolymers were prepared mainly by the copolymerization initiated by small-molecule initiators: 2,2'-azobisisobutyronirile (AIBN) or benzoyl peroxide (BPO) [11].

It seems interesting to examine the possibility of preparation of the copolymers with the application of the functional initiators – macro-azoinitiators, whose molecules are terminated with e.g. hydroxyl groups. Particularly in the case of vinyl monomers, such as styrene or acrylonitrile, when the reaction of chain termination proceeds via the macroradicals recombination [12-14], the telechelic copolymers can be the products of the reaction [15, 16].

The objective of this work was to prepare styrene-acrylonitrile oligomers in the presence of oligomeric functional initiator – 2,2'-azobis[2-methyl-ω-hydroxy-oligo(oxyethylene) propionate] [AIB-OOE(400)], in which the oligooxyethylene chains with hydroxyl functional groups are significant fractions of the macromolecules [17]. Such copolymers, termed as "block-copolymerlike", can be utilized as prepolymers

for the subsequent polyreactions, resulting in the modification of the properties of the final products.

Results and discussion

The kind and chemical structure of the initiator molecule have a influence on the course of radical copolymerization and the mutual reactivity of the comonomers. In order to estimate the monomer reactivity ratios, the compositions of the oligovinyl fragment in S-AN copolymers were determined on the basis of absorption measurements (A_S and A_{AN}) for the bands at established wave numbers by means of the base line method using a previously determined calibration curve A_S/A_{AN} = f([S]/[AN]), for the mixtures of styrene and acrylonitrile homopolymers. Subsequently the instantaneous copolymer composition was obtained by measurement of the ratio of these absorbing bands in the copolymers.

The values of the monomer reactivity ratios (r_S and r_{AN} for styrene and acrylonitrile, respectively) were calculated according to the Kelen–Tüdős method by the composition equation [18]:

$$\eta = \left(r_S + \frac{r_{AN}}{\alpha} \right) \cdot \xi - \frac{r_{AN}}{\alpha} \tag{1}$$

where η and ξ are variables defined as:

$$\eta = \frac{x(y-1)}{\alpha y + x^2} \; ; \; \xi = \frac{x^2}{\alpha y + x^2} \tag{2}$$

whereas α is a auxiliary parameter:

$$\alpha = \frac{x_{min} \cdot x_{max}}{\sqrt{y_{min} \cdot y_{max}}} \tag{3}$$

x denotes the initial composition of the monomers in the reaction mixture ($[S]_0/[AN]_0$), y is the composition of the copolymer expressed in terms of the molar fractions of monomer units in the copolymer (d[S]/d[AN]).

Equation (1), with such defined variables η and ξ, serves for determination of the reactivity ratios at low conversion of the monomers. However, the parameter z defined by Equation (4) should be taken into account at high conversion (extended Kelen-Tüdős method) [19-21]:

$$z = \frac{\lg \dfrac{[S]}{[S]_0}}{\lg \dfrac{[AN]}{[AN]_0}} = \frac{\lg(1 - \zeta_S)}{\lg(1 - \zeta_{AN})} \tag{4}$$

where ζ_S and ζ_{AN} are the partial conversions of particular monomers:

$$\zeta_{AN} = w \frac{\mu + x_0}{\mu + y} \quad \text{and} \quad \zeta_S = \frac{y}{x_0} \zeta_{AN} \tag{5}$$

in which w designates a weight conversion, $\mu = \mu_{AN} / \mu_S$ – ratio of the molecular weights of monomers – acrylonitrile and styrene, respectively, x_0 – initial composition of the monomers mixture.

Authors of the above method, Kelen and Tüdős, have also defined an average value of the monomers composition $\bar{x}$, by the y and z values as consistent with the current conversion:

$$\bar{x} = \frac{y}{z} \tag{6}$$

the application of which in Equation (1) instead of x, through the calculation of variables η and ξ, expressed as follows:

$$\eta = \frac{z(y-1)}{\alpha z^2 + y} \qquad \text{and} \qquad \xi = \frac{y}{\alpha z^2 + y} \tag{7}$$

allowed the determination of the reactivity ratios r_S and r_{AN} in the investigated process (Fig. 1). Because it is a graphical method, correctness of the assumed mechanism can be immediately ascertained by the linearity of the points in the plot $\eta = f(\xi)$.

Tab. 1. Composition of the reaction mixture ($[M]_0$ = 2.5 mol·dm^{-3}, $[I]_0$=0.04 mol·dm^{-3}) and characteristics of copolymers.

Copolymer	$[S]_0/[AN]_0$ [a] (mol·mol^{-1})	d[S]/d[AN] [b] (mol·mol^{-1})	Conversion (wt %)	$\bar{M}_n$ (g·mol^{-1})	T_g (°C)
SAN 1	9.081	4.102	33.0	3600	63.6
SAN 2	4.000	4.040	33.1	3800	58.6
SAN 3	2.305	1.318	46.6	3720	74.3
SAN 4	1.500	1.010	45.9	5000	75.7
SAN 5	1.000	0.732	41.6	7200	81.4
SAN 6	0.668	0.555	47.6	4500	80.0
SAN 7	0.426	0.430	48.5	5000	82.0
SAN 8	0.110	0.233	17.0	4800	71.9

[a] initial ratio of monomers in the reaction mixture (x_0)
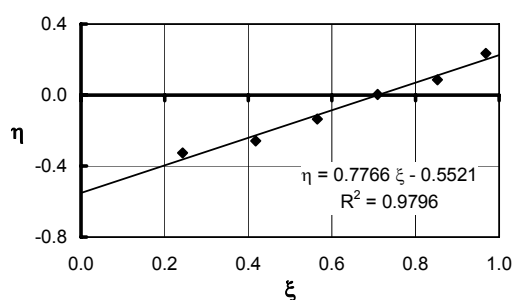[b] ratio of monomer units in copolymer (y)

Fig. 1. Kelen–Tüdős plot for determination of the reactivity ratios in the copolymerization of acrylonitrile and styrene.

The values of reactivity ratios r_S = 0.225 and r_{AN} = 0.722 were determined and the rectilinear dependence η = f(ξ) (Fig. 1) confirms the rightness of the assumed calculation method (according to the terminal model). The obtained results are associated with the presence of azoester AIB-OOE(400) in the reaction system. The oligoether chains of the AIB-OOE(400) can be the matrix ordering the AN monomer

and by this means they accelerate the acrylonitrile addition both to the macroradical ended with the same unit (causing a growth of r_{AN}), and the styrene unit (decreasing value of r_S).

On the basis of the changes in the reactivity ratios of comonomers depending on the copolymerization environment, one can expect the changes in the sequences distribution in the copolymer. Moreover, knowledge of the reactivity ratio values under the specified conditions enables such a design of the monomers mixture composition in order to obtain the copolymer with appropriate composition and properties (Fig. 2, Table 1).
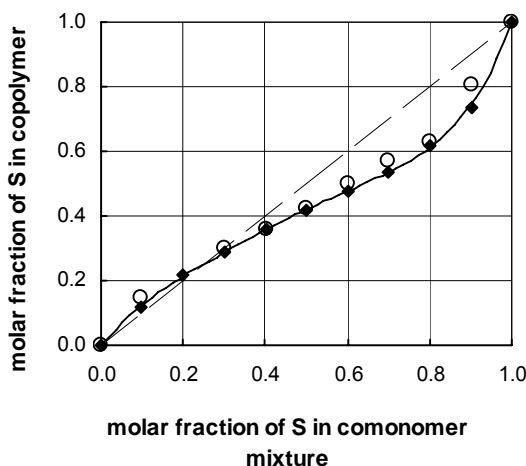

Fig. 2. Dependence of the copolymer composition on the composition of monomers mixture: ♦ – points evaluated for established values of r_S = 0.225 and r_{AN} = 0.722; ○ – experimental points

As can be seen (Table 1), the small values of the copolymer molecular weights testify about the oligomeric products of the syntheses. Moreover the presence of the oligomeric azoester AIB-OOE(400) (as reaction initiator) causes the oligoether chains to be the significant fraction in the copolymer macromolecules. The influence of oligomers composition on their important characteristics – thermal properties [22], was investigated in the temperature range of -50 – 280 °C, by the determination of the glass transition temperatures T_g (Table 1). A single T_g was observed, the value of which increases along with increasing AN fraction in the copolymer. The maximum value (81,4–82,0 °C) was achieved at the molar composition ~60 mol% AN in the copolymer, and then this temperature decreases to ~72°C at 80 mol% AN (Fig. 3).

The results reported in work, for example [9], indicate, that T_g dependence on the composition of SAN copolymer changes in the temperature range 105-117 °C, and reaches a maximum at 50 wt% content of styrene. In the case of PS the T_g value amounts to 102 °C and for PAN – 94 °C.

The decrease of T_g value in the examined ether-acrylonitrile-styrene copolymers, results mainly from the presence of the oligoether chains derived from the initiator AIB-OOE (400) which causes the increase of mobility of the oligomeric chains, as well as due to low molecular weights of the copolymers.
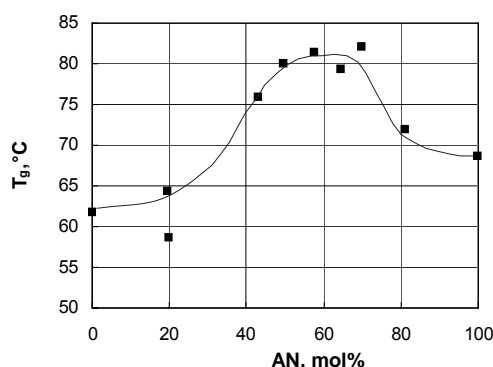
Fig. 3. Dependence of T_g on the composition of styrene-acrylonitrile segment of copolymer macromolecules.
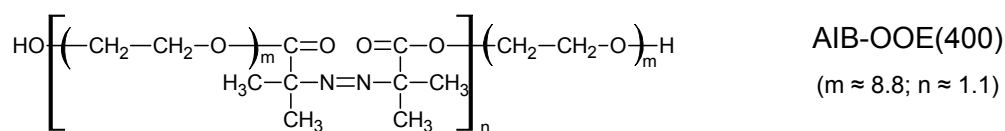
Conclusions

The application of telechelic, oligomeric azoinitiator AIB-OOE (400) in the copolymerization of styrene and acrylonitrile enables the preparation of essentially a three-component product, with a low molecular weight. The products can be utilised for the subsequent polyreactions as prepolymers having the functional groups or as effective compatibilizers in various immiscible polymer systems, simultaneously affecting the change of properties, e.g. an improvement of resistance on solvents or oils.

The AIB-OOE (400) initiator causes the increase of the reactivity ratio of acrylonitrile in the copolymerization with styrene, and the acceleration of the polymerization reaction of acrylonitrile, this being the subject of work published in [23].

Experimental part

The monomers: styrene and acrylonitrile were purified by washing several times with 5% aqueous NaOH solution to remove inhibitors. Subsequently the monomers were neutralised by washing with distilled water, dried over anhydrous $MgSO_4$ and distilled in N_2 under reduced pressure in the presence of hydroquinone and CaH_2. Solvent *N,N*-dimethylformamide (DMF) was purified by rectification carried out at normal pressure. Azoinitiator AIB-OOE(400) with $\overline{M}_n$=1100g·mol^{-1} was prepared by means of modified Pinner's method from AIBN and oligo(oxyethylenediol) with $\overline{M}_n$ = 400g·mol^{-1} [17]:

AIB-OOE(400)

(m ≈ 8.8; n ≈ 1.1)

The copolymerization reaction of styrene and acrylonitrile was carried out in solution at 60 °C under N_2 atmosphere using AIB-OOE (400) as a functional azoinitiator and DMF as a solvent. The overall concentration of the monomers was constant ($[M]_0$ = 2.5 mol·dm^{-3}) and the initiator concentration of $[I]_0$ = 0.04 mol·dm^{-3} was selected for all experiments. The molar fractions of the monomers in the reaction mixture were

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varied in the consecutive syntheses by increasing acrylonitrile fraction. After the reaction had proceeded (360 min) the copolymers were precipitated in methanol/water (90/10 V/V) mixture, purified by redissolution in chloroform, followed by the precipitation and then dried at 40 °C under vacuum to a constant mass.

The copolymer compositions were determined by IR spectroscopy (Specord M80 with application of software) utilising the characteristic absorption bands for styrene (3028 cm^{-1}) and acrylonitrile (2240 cm^{-1}) monomer units. The molecular weights of copolymers were determined by vapour pressure osmometry (VPO Knauer, operating range of molecular weights: 40-35000 $g \cdot mol^{-1}$), in DMF as a solvent at temperature of 100 °C. The thermal properties were examined by differential scanning calorimetry (DSC 910 – TA Instruments) under N_2 atmosphere at a heating rate of 10 °C·min^{-1}.

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