

# Synthesis and some solution properties of block copolymer styrene—acrylonitrile

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Styrene—acrylonitrile block copolymers were synthesized by emulsion polymerization at 30°C, in which peroxide of powdered isotactic polypropylene as a heterogeneous initiator, disodium salt of ethylenediaminetetraacetic acid as an activator, and Slovasol 2430 as a nonionic emulsifier were used. For the preparation of the block copolymer one of the characteristic properties of the mentioned polymerization system, *i.e.* the existence of long-living polystyrene radical in emulsion was evaluated. After removing of the initiator the first monomer — styrene was polymerized up to a certain conversion and then acrylonitrile was added to the growing polystyrene radicals. A block copolymer was formed, which contained a pure polystyrene block and an acrylonitrile sequence with fragments of styrene. The obtained copolymers with various styrene—acrylonitrile ratio were characterized by IR spectroscopy. By means of viscometry and light scattering some of their properties in methyl ethyl ketone and *N,N*-dimethylformamide were studied.

Блок-сополимеры стирола и акрилонитрила были получены посредством эмульсионной полимеризации при 30°C, в которой применялись перекись порошкообразного изотактического полипропилена в качестве гетерогенного инициатора, двунариевая соль этилендиаминтетрауксусной кислоты в качестве активатора и Словасол 2430 в качестве неионного эмульгатора. В целях получения блок-сополимера оценивалось одно из характеристических свойств упомянутой полимеризационной системы, а именно присутствие долгоживущих полистирольных радикалов в эмульсии. После устранения инициатора первый мономер — стирол — полимеризовался до определенной степени конверсии, а затем к растущим полистирольным радикалам добавлялся акрилонитрил. Образовывался блок-сополимер, содержащий чисто полистирольный блок и акрилонитрильную цепь с фрагментами стирола. Полученные сополимеры с различным соотношением стирола и акрилонитрила были охарактеризованы с помощью ИК-спектроскопии. Посредством вискозиметрии и светорассеяния изучались некоторые их свойства в метилэтилкетоне и *N,N*-диметилформамиде.

It is known [1] that the heterogeneous initiated emulsion polymerization of styrene has a living nature. This polymerization may be arranged so that the polymeric initiator — oxidized isotactic polypropylene powder — could be removed from the emulsion during the polymerization. In the mentioned case the polymerization proceeded without change of the rate, the molecular mass of the polymer continuously increased with conversion up to a high value and the molecular mass distribution was narrow. The existence of long-living radicals in the emulsion polymerization of styrene was utilized by *Horie* and *Mikulášová* [2] for the preparation of diblock copolymers of styrene and methyl methacrylate. The same initiator system was also applied for the synthesis of triblock copolymers containing the sequence styrene, *p*-*tert*-butylstyrene, styrene [3].

In this paper we refer to the preparation of copolymer styrene—acrylonitrile by emulsion polymerization with a heterogeneous polymeric initiator and an amine type of activator. We describe also some initial results which have been obtained by light scattering and viscometry measurements of styrene—acrylonitrile copolymers with different mole ratio of acrylonitrile and styrene.

## Experimental

*Isotactic polypropylene* (PP) was isolated from commercial polypropylene powder (Slovnaft, Bratislava) by extraction of atactic material with hot heptane. Polypropylene was oxidized with oxygen containing ozone for 2 h at room temperature. The hydrogen peroxide content ( $n(\text{O}_2)/m(\text{PP})$ ) determined iodometrically was  $1.9 \times 10^{-2} \text{ mol kg}^{-1}$  [4].

*Styrene* monomer was washed with sodium hydroxide solution and water. Then it was dried over calcium chloride, twice distilled under reduced pressure in nitrogen and used immediately.

*Acrylonitrile* was twice distilled in  $\text{N}_2$  atmosphere just before polymerization.

Anal. grade disodium salt of ethylenediaminetetraacetic acid ( $\text{EDTA}$ ) and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  dissolved in water ( $c = 4.0 \times 10^{-2} \text{ mol dm}^{-3}$ ) in amount of substance ratio 1 : 1 were used as activator. As emulsifier was used an aqueous solution of nonionic emulsifier type Slovasol 2430 with the empirical formula  $\text{CH}_3(\text{CH}_2)_{23}(\text{C}_2\text{H}_4\text{O})_{29}\text{C}_2\text{H}_4\text{OH}$  ( $c = 0.145 \text{ mol dm}^{-3}$ ).

Water was redistilled in glass. All solutions and water were kept in nitrogen atmosphere. All used solvents were anal. grade. Benzene was dried with  $\text{CaCl}_2$  and fractionally distilled. Methyl ethyl ketone and *N,N*-dimethylformamide were twice distilled before use.

## Polymerization

Styrene—acrylonitrile copolymer was prepared by emulsion polymerization in a special glass reactor described in a previous paper [2]. All procedures were carried out

under a flow of purified nitrogen. The initiator — oxidized polypropylene — was put into the reaction vessel and evacuated, then the aqueous solution of activator and emulsifier were added in inert atmosphere. The system was stirred and after 5 min at 30 °C styrene was added into the reactor. The polymerization of the first monomer in the presence of the initiator was carried out for 10 min or 15 min, then the initiator was separated from the emulsion by filtration through a sintered glass filter. Polymerization proceeded up to the high conversion of styrene in the second part of the reactor without initiator. After a certain time acrylonitrile was added to the emulsion. The formation of copolymer in the system was traced by the analysis of samples which were taken with a syringe through a rubber stopper.

The isolation of the block copolymer from the homopolymer was made by the selective precipitation technique. The prepared samples were dissolved in benzene at room temperature during 48 h. Homopolystyrene (HPS) dissolved and styrene—acrylonitrile (SAN) copolymer, which was only swelled (up to the certain mole fraction of styrene) could be separated by filtration or centrifugation. Homopolystyrene was precipitated from benzene solution by methanol. The separated SAN copolymer was purified by precipitation from *N,N*-dimethylformamide/methanol system.

### *IR spectra*

The composition of the block copolymers was determined by infrared analysis with an IR-20 type spectrometer (Zeiss, Jena). Absorbances at  $\tilde{\nu} = 760 \text{ cm}^{-1}$  for styrene units and  $\tilde{\nu} = 2300 \text{ cm}^{-1}$  for acrylonitrile units were used for the calculation. A mixture of known amounts of polystyrene and polyacrylonitrile was employed as a standard.

### *Viscometry*

The viscometry of the solutions was measured at 30 °C with Ubbelohde diluting capillary viscometer and corrected for the kinetic energy effects. Butanone and *N,N*-dimethylformamide were used as solvents. The limiting viscosity number  $[\eta]$  and the Huggins constant  $k_H$  were determined in the usual way from the equation

$$\frac{\eta - \eta_0}{\eta_0 \rho} = [\eta] + k_H [\eta]^2 \rho + \dots \quad (1)$$

$\eta$  and  $\eta_0$  denote the viscosity of solution and solvent, respectively,  $\rho$  is the solution mass concentration.

### *Light scattering*

Optically pure dilute solutions of copolymers in *N,N*-dimethylformamide were investigated using a commercial Sofica photometer at 25 °C with unpolarized light of

wavelength 546.1 nm. The refractive index increments of copolymers ( $v_{\text{cop}}$ ) were calculated from  $v_{\text{PS}}$  of polystyrene ( $v_{\text{PS}} = 0.165 \text{ cm}^3 \text{ g}^{-1}$ ) and from  $v_{\text{PAN}}$  of polyacrylonitrile ( $v_{\text{PAN}} = 0.089 \text{ cm}^3 \text{ g}^{-1}$ ) in *N,N*-dimethylformamide [5] according to the equation

$$v_{\text{cop}} = x_{\text{PS}} \cdot v_{\text{PS}} + (1 - x_{\text{PS}})v_{\text{PAN}} \quad (2)$$

where  $x_{\text{PS}}$  is the mole fraction of polystyrene in block copolymer. Light scattering measurements were carried out in the range of angles from  $30^\circ$  to  $90^\circ$  with the increment  $5^\circ$ . The data from light scattering measurements were evaluated by the Zimm method in a similar way as in the previous works [6].

## Results and discussion

The block copolymers with various ratio of styrene and acrylonitrile were prepared by emulsion polymerization initiated by peroxides of powdered isotactic polypropylene. For this case the complex activator of the type  $\text{Fe}^{2+}$ —EDTA was used. In its presence the decomposition of the initiator proceeds more effectively [7], which leads to the increase of the polymerization rate. The influence of copolymerization conditions on the copolymer composition is shown in Table 1. There is not quoted the total conversion of copolymer because this value obtained directly after the synthesis was influenced by the presence of homopolystyrene. During the careful separation of the copolymer from HPS, particularly at higher polystyrene content in the samples, the dissolution of a certain part of the copolymer occurred, which misrepresented the yield values.

On the basis of the previous knowledge [2, 3] it was expected that after the removal of the initiator and after the total styrene polymerization a block copolymer would be formed when acrylonitrile was added into the system. But it has been shown that acrylonitrile polymerizes in the mentioned system at  $30^\circ\text{C}$  only with a very slow rate. The formation of the copolymer occurs only when acrylonitrile is added to the system, which contains still a certain amount of unpolymerized styrene (Table 1, samples 2—6). In such a case a block copolymer is formed, which contains a pure polystyrene block, on which the polyacrylonitrile sequence with styrene fragments is bonded. The acrylonitrile fraction in the copolymer increases with the polymerization time, which is indicated by the IR spectrum of the sample No. 3 and No. 6 (Fig. 1).

The purified SAN copolymers were characterized by viscometry and by light scattering. For the viscometry two solvents were used: methyl ethyl ketone (MEK) and *N,N*-dimethylformamide (DMF). The dependence of  $[\eta]$  and Huggins parameter  $k_{\text{H}}$  on the mole fraction of polyacrylonitrile in the copolymer ( $x_{\text{AN}}$ ) is shown in Fig. 2. In DMF, which is a relatively good solvent for both components of the copolymer, an increase of  $[\eta]$  with the increasing content of AN was observed. This result was expectable. This is due to the characteristic

Table 1

The influence of the copolymerization conditions on the composition of SAN block copolymer

No.	Polymerization time of S without initiator*	Conversion of S (before addition of AN)	Polymerization time of the system after addition of AN	Composition of copolymer after separation from HPS	
	min			%	min
1	60	98.1	40	1.00	0
2	40	85.0	60	0.77	0.23
3	30	69.2	90	0.72	0.28
4	↓	↓	150	0.51	0.49
5	↓	↓	190	0.41	0.59
6	↓	↓	290	0.25	0.75

The composition of polymerization system:

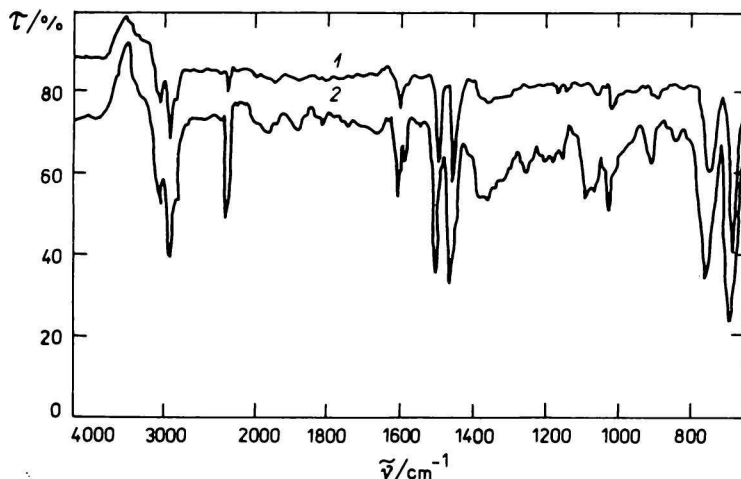
Initiator: oxidized powdered polypropylene

$$n(O_2)/m(PP) = 1.9 \times 10^{-2} \text{ mol kg}^{-1}$$

Activator:  $FeSO_4$ —disodium salt of ethylenediaminetetraacetic acid (EDTA), amount of substance ratio 1:1 ( $c(FeSO_4 \text{ in em}) = 1.94 \times 10^{-3} \text{ mol dm}^{-3}$ )Emulsifier:  $c(\text{Slovasol 2430 in em}) = 6.54 \times 10^{-2} \text{ mol dm}^{-3}$ 

Temperature = 30 °C.

\* The polymerization time of the first monomer (S) with the initiator was 15 min (No. 1, 2) and 10 min (No. 3–6).

Fig. 1. Infrared spectra of styrene—acrylonitrile copolymer with  $x_{AN} = 0.28$  (1) and  $x_{AN} = 0.75$  (2).

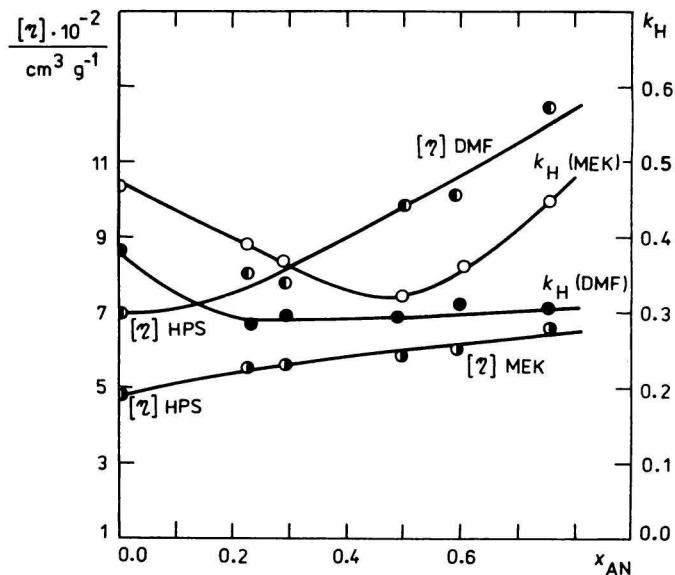


Fig. 2. Variation of the limiting viscosity number  $[\eta]$  and Huggins parameter  $k_H$  in methyl ethyl ketone (MEK) and *N,N*-dimethylformamide (DMF) at 30°C with the mole fraction of polyacrylonitrile in block copolymer SAN.

properties of the used polymerization system, *i.e.* the existence of long-living polystyrene radicals in the emulsion [8]. The addition of acrylonitrile during the polymerization of styrene leads to the growing of chains enriched with this monomer, which in the absence of the termination reactions, is manifested by the increase of molecular mass. Another behaviour is displayed by the block SAN copolymer in MEK, which is a good solvent for PS, but not for PAN. In this case  $k_H$ , as a function of  $x_{AN}$ , goes through a minimum. It is possible to assume that the chains containing PAN will try to occupy the smallest volume but as long as the PS sequence is in preponderance the tendency to the chain expansion will prevail. Therefore the block SAN copolymers will behave in MEK approximately up to  $x_{AN} = 0.5$  rather like HPS. When the acrylonitrile component in the copolymer preponderates simultaneously with the growth of the molecular mass the copolymer is acquiring the properties of PAN and MEK is becoming a worse solvent.

The characterization of block SAN copolymers by light scattering was made in DMF. Already from the viscometric measurements it was possible to infer that the synthesized copolymers would have a high relative molecular mass. This was also shown by the nonlinear dependences of  $K\varrho/R_\theta = f(\varrho)$ , resp.  $\sin^2 \Theta/2$ , particularly at angles higher than  $75^\circ$ . Similar courses of the mentioned dependences were also obtained during the measuring of extremely high molecular

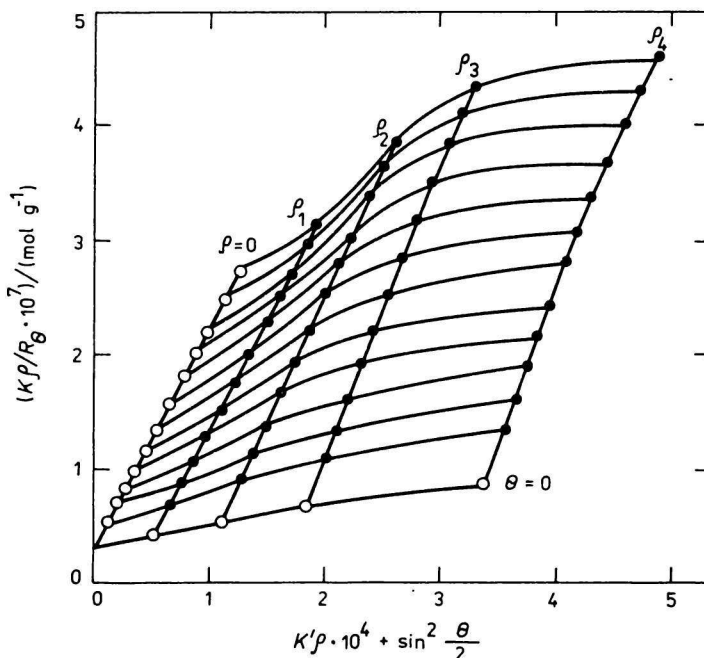


Fig. 3. Zimm plot of block copolymer styrene—acrylonitrile (sample No. 4) in DMF at 25°C.

Concentration of solution:

$$\begin{aligned} \rho_1 &= 0.631 \times 10^{-4} \text{ g cm}^{-3} & \rho_3 &= 2.209 \times 10^{-4} \text{ g cm}^{-3} \\ \rho_2 &= 0.126 \times 10^{-4} \text{ g cm}^{-3} & \rho_4 &= 3.031 \times 10^{-4} \text{ g cm}^{-3} \end{aligned}$$

polystyrene in toluene [6]. It is proposed, similarly as by the light scattering of other polymers [9] with  $\bar{M}_{r,w}$  higher than  $10^7$ , to work at angles up to  $80^\circ$ . Zimm plot of the SAN copolymer (sample No. 4) is in Fig. 3. The apparent relative molecular mass of this and the other copolymers was of the order  $10^6$  to  $10^7$ . The variation of  $\bar{M}_{r,ap}$  and of the gyration radius ( $\bar{R}_{G,ap}$ ) with increasing acrylonitrile fraction in the copolymer is demonstrated in Fig. 4. It has been shown that with increasing of the AN component in the copolymer also the values of both studied parameters increased. This is in connection, as it was mentioned previously, with the positive effect of the polymerization time on the growth of the degree of polymerization. It is possible to assume that the values  $\bar{R}_{G,ap}$  will influence to a certain degree also the interaction between copolymer and solution. In consequence of this it is possible that in DMF can occur a more marked expansion mainly of those chains of block copolymers, in which the polyacrylonitrile component prevails. This consideration could be also supported by the simultaneously observed alleviation of the decreasing of the second virial coef-

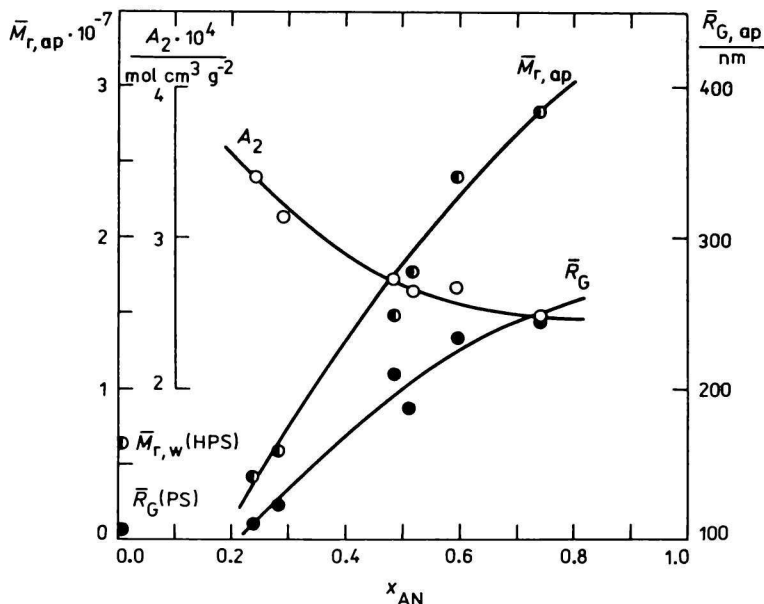


Fig. 4. Dependence of the apparent radius of gyration ( $\bar{R}_{G,ap}$ ), apparent relative molecular mass ( $\bar{M}_{r,ap}$ ), and the second virial coefficient ( $A_2$ ) of block copolymers SAN in DMF on the mole fraction of polyacrylonitrile.

ficient  $A_2$  with the increasing of  $x_{AN}$  above the value of 0.5. Therefore, further light scattering measurements in several selective solvents will be needed for the more detailed considerations of the question to what extent the studied parameters are influenced by the change of the copolymer composition with the polymerization time.

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