

Naphthalene photoinitiated copolymerization of unsaturated monomers

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For the naphthalene photoinitiated copolymerization of acrylonitrile with styrene, methyl methacrylate, vinyl chloride, vinyl acetate, and isoprene the copolymerization parameters, number average molecular weights, and limiting viscosity numbers of copolymers were determined. It was found that copolymerization rates increased by increasing the acrylonitrile concentration in feed. The results obtained point at the radical nature of copolymerization.

При нафталином фотоинициированной сополимеризации акрилонитрила со стиролом, метилметакрилатом, винилхлоридом, винилацетатом и изопреном были установлены параметры сополимеризации, средний молекулярный вес и предельная характеристика вязкости сополимеров. Было установлено, что скорость сополимеризации увеличивается с повышением концентрации акрилонитрила в затравке. Полученные результаты указывают на радикальную сущность сополимеризации.

In our papers [1—3] we have shown that aromatic hydrocarbons photoinitiated the polymerization of acrylonitrile. It was concluded that polymerization proceeds by a free radical mechanism. As initiating particles the ion radicals were considered. These initiating particles were formed in the subsequent reactions of the reaction product arising in the interaction between aromatic hydrocarbon in the first excited singlet state and acrylonitrile in the ground state.

In this communication we report the results of study of copolymerization of acrylonitrile (AN) with methyl methacrylate (MMA), styrene (S), vinyl chloride (VCl), vinyl acetate (VAc), and isoprene (I) in the presence of naphthalene (N) acting as photoinitiator.

Experimental

Monomers, all commercial products were carefully purified by three times repeated rectification under reduced pressure of argon. Vinyl chloride was dried by passing it through silica gel column. No further attempts were made to purify it. Isoprene (Koch and Light

Ltd.) was used without any further purification. Naphthalene (Lachema, Brno) was a zonally refined chemical. A description of samples preparation for polymerization and copolymerization as well as of the irradiation equipment was given elsewhere [2]. For irradiation, a medium pressure mercury lamp 250 W (Tesla Holešovice, Prague) emitting radiation of the wavelengths: 253.6 (69.9), 265.4 (39.8), 296.7 (39.8), 302 (56.6), 312.6 (92.0), 313.2 (61.9), 334.1 (26.5), 365.0 (100), 365.5 (46.0), 404.7 (63.7), 407.8 (24.8), 435.8 (81.4), 546.1 (47.8), 577.0 (41.6), 579.0 (26.5) nm was used. The radiation of the wavelengths $\lambda < 310$ nm was filtered off by using Pyrex filter. The composition of copolymers was determined on the basis of the results of elementary analysis (C, H, N). The content of chlorine in copolymers was determined according to *Schöniger* method [4]. All copolymerizations were carried to low degrees of conversion ($< 8\%$) and at 45°C . For acrylonitrile—vinyl chloride copolymerization temperature of 15°C was used. Molecular weights of copolymers were measured on the Hewlett—Packard, Model 502, High Speed Membrane osmometer. Limiting viscosity numbers of polymers and copolymers were determined by extrapolation of η_{sp}/c to zero concentration. Flow times of dilute polymer and copolymer solutions were measured by Ubbelohde viscometer.

Results and discussion

The absorption spectra of monomers used are given in Fig. 1. The results of polymerization of various monomers in the presence of naphthalene are given in Fig. 2.

Details of the polymerization of acrylonitrile photosensitized by naphthalene are given elsewhere [1, 2]. From the monomers used, only styrene polymerizes under the action of naphthalene and u.v. light of the wavelength $\lambda \geq 310$ nm, with a polymerization rate exceeding several times the rate of thermal (dark) polymerization of styrene. Other monomers do not polymerize at all under given reaction conditions. The observed VCl polymerization is probably caused by impurities present in VCl. In the mixtures acrylonitrile (1)—comonomer (2) the copolymerization rate is a function of composition of monomers in feed (Fig. 3).

The course of copolymerization rate in dependence on the feed composition reflects in the case of AN—S that also styrene participates in the initiation process. This is confirmed also by results found for the system styrene—naphthalene (Fig. 2). The rapid increase in copolymerization rate for [AN] 90 mole % in feed is a consequence of the copolymerization proceeding in heterogeneous medium. (Copolymer formed precipitates from the mixture of comonomers.)

Irrespective of the feed composition, the copolymerizations proceed under heterogeneous conditions for the systems AN—VCl and AN—VAc. The conversion curves for acrylonitrile copolymerization with various monomers are linear up

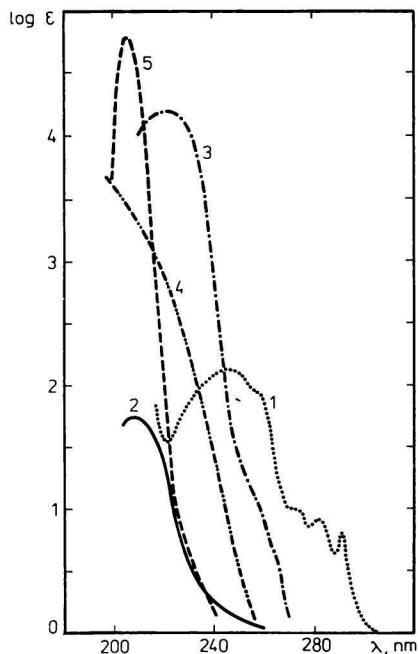


Fig. 1. Absorption spectra of various monomers in ethanol.

1. S; 2. MMA; 3. I; 4. VAc; 5. AN.

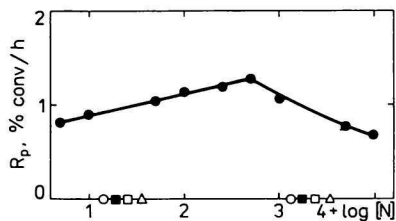


Fig. 2. Dependence of the polymerization rate ($\% h^{-1}$) on concentration of naphthalene.

● S; ○ MMA; ■ I; □ VAc; △ VCl.

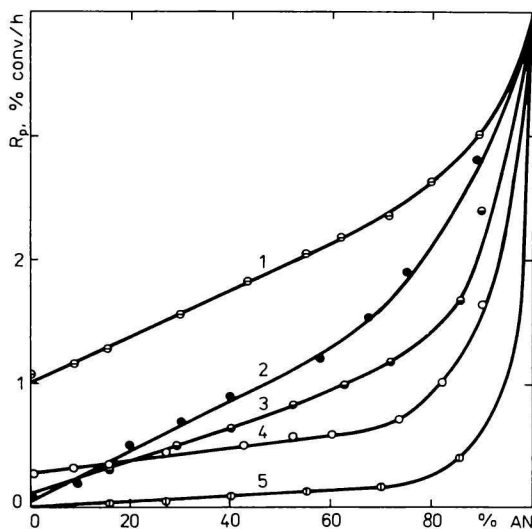


Fig. 3. Dependence of the copolymerization rate ($\% h^{-1}$) on concentration of acrylonitrile in feed.

1. AN-S; 2. AN-VAc; 3. AN-MMA; 4. AN-VCl; 5. AN-I.

Table 1

Concentration of acrylonitrile (in mole %) in mixture of comonomers (A) and copolymers (B)

| Comonomer | A | B | $M_n \cdot 10^{-5}^a$ | $[\eta]^b$ dl g ⁻¹ |
|---------------------|-------|-------|-----------------------|----------------------------------|
| Styrene | 8.45 | 22.50 | 3.49 | 1.19 |
| | 16.24 | 26.50 | 4.00 | 2.05 |
| | 30.35 | 33.50 | — | 2.75 |
| | 53.70 | 45.00 | 6.26 | 3.15 |
| | 63.50 | 47.00 | 4.33 | 3.20 |
| | 72.40 | 50.00 | 5.32 | 3.25 |
| | 80.26 | 53.50 | 9.08 | 3.50 |
| | 87.50 | 56.00 | 3.59 | 3.45 |
| Vinyl chloride | 8.49 | 51.50 | 1.04 | 2.10 |
| | 15.65 | 57.00 | 0.81 | 2.20 |
| | 27.07 | 64.50 | 0.47 | 2.10 |
| | 42.59 | 75.00 | 0.64 | 2.50 |
| | 52.70 | 79.00 | 1.31 | 4.00 |
| | 60.00 | 84.00 | 1.12 | 4.50 |
| | 73.60 | 90.00 | 1.41 | 4.75 |
| | 82.30 | 93.50 | 1.45 | 5.25 |
| Methyl methacrylate | 7.90 | 6.50 | 6.16 | 1.90 |
| | 15.20 | 12.50 | 5.92 | 2.20 |
| | 28.70 | 21.50 | 5.32 | 2.10 |
| | 40.90 | 27.00 | 5.81 | 2.40 |
| | 51.80 | 31.50 | 5.27 | 2.40 |
| | 61.70 | 34.00 | 6.10 | 2.40 |
| | 70.80 | 41.00 | 2.17 | 2.20 |
| | 86.60 | 63.00 | 2.00 | 2.50 |
| Isoprene | 14.50 | 29.50 | — | — |
| | 27.50 | 34.00 | — | — |
| | 41.50 | 40.00 | — | — |
| | 55.00 | 44.00 | — | — |
| | 69.00 | 47.00 | — | — |
| | 85.50 | 55.00 | — | — |
| Vinyl acetate | 10.00 | 40.00 | — | — |
| | 20.00 | 60.00 | — | — |
| | 40.00 | 80.50 | — | — |
| | 58.50 | 87.50 | — | — |
| | 76.50 | 94.50 | — | — |
| | 88.00 | 96.50 | — | — |

a) Number average molecular weight, in *N,N*-dimethylformamide at 30°C.b) In *N,N*-dimethylformamide at 25°C.

Table 2

Copolymerization parameters for acrylonitrile (r_1) and various monomers (r_2) in copolymerization photoinitiated by naphthalene

| Comonomer | r_1 | r_2 |
|---------------------|-----------------|-----------------|
| Styrene | 0.06 ± 0.01 | 0.43 ± 0.03 |
| Methyl methacrylate | 0.10 ± 0.04 | 1.23 ± 0.15 |
| Vinyl chloride | 3.14 ± 0.25 | 0.08 ± 0.02 |
| Vinyl acetate | 4.20 ± 0.20 | 0.08 ± 0.02 |
| Isoprene | 0.05 ± 0.10 | 0.36 ± 0.02 |

Table 3

Selective extractions of acrylonitrile copolymers^a

| Comonomer | mole % AN in copolymer | Soluble part of copolymer (%) |
|---------------------|---------------------------|----------------------------------|
| Styrene | 22.5 | 100.0 ^b |
| | 26.5 | 43.0 |
| | 33.5 | 20.0 |
| | 37.5 | 0.0 |
| | 6.5 | 100.0 ^b |
| Methyl methacrylate | 12.5 | 100.0 |
| | 21.5 | 80.0 |
| | 27.0 | 5.0 |
| | 31.0 | 0.0 |
| | 51.5 | 24.0 ^c |
| Vinyl chloride | 57.0 | 4.0 |
| | 64.5 | 0.0 |
| Isoprene | d | d |
| Vinyl acetate | e | e |

a) 2 g of copolymers were extracted by a given solvent (100 cm³) at room temperature. The solvent was removed every 24 h. This procedure was repeated three times.

b) In benzene.

c) In tetrahydrofuran.

d) Only swelling in benzene was observed, but no soluble part of copolymer was detected.

e) The soluble part in benzene was detected in none of the copolymers studied.

to (at least) 2% of conversion (Fig. 4). The relation between feed and copolymer composition as well as number average molecular weights and limiting viscosity numbers of copolymers are given in Table 1.

Using the data of Table 1 and the method of *Fineman and Ross* [5] the copolymerization parameters were calculated (Table 2). The found values of

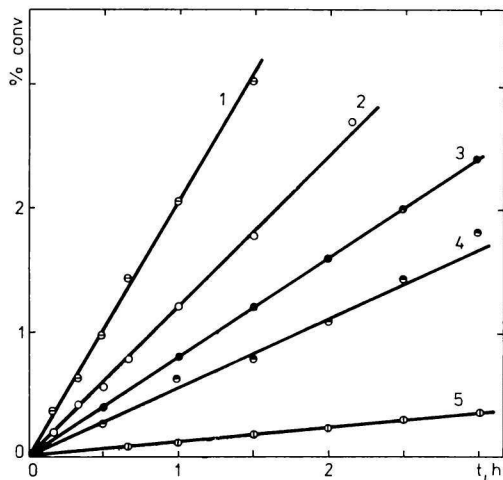


Fig. 4. Conversion in acrylonitrile copolymerization (%) as a function of reaction time.

1. AN—S 54 mole % in feed ; 2. AN—VAc 58 mole % in feed ; 3. AN—MMA 52 mole % in feed ;
4. AN—VCl 53 mole % in feed ; 5. AN—I 55 mole % in feed.

copolymerization parameters (Table 2) give further evidence about the radical nature of the copolymerization process photoinitiated by naphthalene. Further results of the study of acrylonitrile copolymerization photoinitiated by naphthalene will be reported elsewhere [6].

For further characterization the selective extractions of copolymers with benzene (acrylonitrile—styrene, acrylonitrile—methyl methacrylate, acrylonitrile—iso-prene, acrylonitrile—vinyl acetate) and with tetrahydrofuran (acrylonitrile—vinyl chloride) were performed. The results are summarized in Table 3.

References

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