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Thermal behaviour of the copolymers of acrylonitrile with methyl acrylate and itaconic acid or its derivatives

Andrei V. Shlyakhtin,* Dmitrii A. Lemenovskii and Ilya E. Nifant'ev

Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation.
Fax: +7 495 939 1671; e-mail: shlyahtinav@mail.ru

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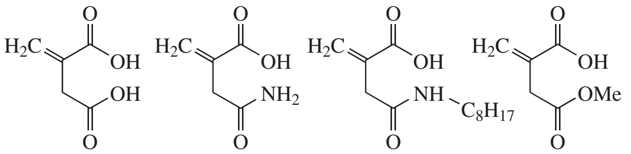
Itaconic acid monoesters and monoamides, such as 2-carbamoylmethacrylic acid, *N*-octyl-2-carbamoylmethacrylic acid and 2-methoxycarbonylmethacrylic acid, smoothed the peak of heat release upon the thermal cyclization of acrylonitrile copolymers with commensurable effectiveness, and they can serve as competitive substitutes for itaconic acid in the synthesis of carbon fiber precursors.

The production of carbon fibers is an important area of applications of acrylonitrile-containing copolymers; on a global scale, 90% carbon fibers are produced with the use of these copolymers. In this case, homo-polyacrylonitrile (homo-PAN) is not used for the production of carbon fibers because of a sharp exothermic effect at the first stage of the heat treatment of the polymer (PAN precursor), when the cyclization of nitrile groups occurs to finally impair the quality (strength) of the carbon fiber obtained. To solve this problem, comonomers (acids which smooth the peak of heat release) are introduced into the PAN precursor. For this purpose, itaconic, acrylic and methacrylic acids are most frequently used. In addition to acid comonomers, neutral comonomers such as methyl acrylate (MA) and methyl methacrylate are introduced into the PAN precursor to improve the plasticity of the copolymer.[1–3]

Recently, the use of the mono- and biderivatives of itaconic acid (the monoalkyl esters of itaconic acid, the methyl ester of 3-aminocarbonylbut-3-enoic acid and the methyl ester of 3-carbamoylbut-3-enoic acid) as comonomers instead of itaconic acid was reported. The experimental data demonstrated that, qualitatively, the copolymers obtained are highly competitive with copolymers with itaconic acid in terms of their capability for thermal cyclization.[4–7] In this case, a systematic comparison between the thermal cyclization parameters of copolymers with itaconic acid and copolymers based on itaconic acid monoesters and monoamides obtained under identical conditions was not reported in the literature. Due to the presence of two carboxyl groups in itaconic acid, it is possible to vary the structure of its derivatives over a wide range with the retention of an acidic fragment. In this study, we compared the thermal behaviours of homo-PAN and acrylonitrile copolymers with MA and itaconic acid **1** and also with its mono derivatives: 2-carbamoylmethacrylic acid **2**, *N*-octyl-2-carbamoylmethacrylic acid **3** and 2-methoxycarbonylmethacrylic acid **4**.[†] All of the copolymers were obtained under identical conditions by solution polymerization which provided the precise control of temperature and homogeneity of the reaction mixture.[‡]



1 **2** **3** **4**

The molecular-weight characteristics and the composition of the obtained polymers were determined by gel filtration chromatography and ^{1}H NMR spectroscopy, respectively. Table 1 indicates that the itaconic comonomers are inserted to approximately the same degrees. In this case, the yield of a copolymer with itaconic

Table 1 Composition and molecular-weight characteristics of test polymers.

Co-mono-mer	Initial composition (mol%)			Composition (mol%)^b		Yield (%)	M_n^c	PD^c
	Acrylo-nitrile	MA	Comono-mer	MA	Comono-mer			
–^{a}	100	–	–	–	–	71	47 800	2.38
1	97	2	1	1.7	1.2	57	42 600	2.34
2	97	2	1	1.7	0.9	69	41 800	2.19
3	97	2	1	1.6	1.2	79	46 300	2.10
4	97	2	1	1.6	0.9	70	46 100	2.20

^{a}Homo-PAN. ^{b}The concentrations of comonomers were determined by the integration of signals in the ^{1}H NMR spectra of copolymers (solvent, DMSO-d_6): the methylene group of a polymer chain (br., 2.23–1.82 ppm), the methyl group of MA (3.69 ppm), the methyl group of **4** (3.59 ppm), the methyl group of **3** (0.85 ppm) and the amide group of **2** (7.58, 6.83 ppm). For the determination of the itaconic acid **1** content, the solution of a polymer in DMSO-d_6 was treated with an Et_2O solution of diazomethane and evaporated *in vacuo*, and the concentration of methylated carboxyl groups was determined as in the case of MA. ^{c}Mn is the number-average molecular weight, and PD is polydispersity. Analysis was conducted on a GPC-120 chromatograph from PolymerLabs at 50 °C in DMF containing 0.1 wt% LiBr at a flow rate of 1 cm^3 min^{-1}. For the separation, two columns PLgel 5 m MIXED B [$M = (5\times10^2)–(1\times10^7)$] were used. The solution of a polymer in the eluent with a polymer concentration of 1 mg cm^{-3} was prepared for the analysis. Calibration was performed with standard PMMA samples.

[†] The structures of compounds **2**–**4** were determined by ^{1}H NMR spectroscopy (Bruker Avance 400 instrument, $CDCl_3$ solutions). Compounds **2**–**4** were synthesized employing published procedures.[8–10] As the starting reagent for the synthesis, itaconic anhydride was used, which was prepared as follows: 10.0 g of itaconic acid (Aldrich, 99%) and 50 ml of thionyl chloride were placed in a 100-ml round-bottom flask. A reflux condenser with a calcium chloride tube was attached to the flask, and the contents of the flask was stirred on boiling (76 °C) for 6 h. The homogeneous reaction mixture was cooled and added to a tenfold amount of carbon tetrachloride. The crystals formed were washed with CCl_4 (3×50 ml) and dried on a glass filter and then *in vacuo*. Yield, 5.51 g (64%).

[‡] *Synthesis of homo-PAN*. A magnetic anchor, 9.3 ml of DMSO, 3.0 ml (0.046 mol) of acrylonitrile and 7.5 mg of azo(bis)isobutyronitrile (AIBN) were placed in a 15-ml glass ampoule. The ampoule was filled with argon and sealed. Then, the ampoule was kept at 70 °C for 6 h and opened; the resulting polymer solution was poured out into water, and the obtained polymer was filtered off.

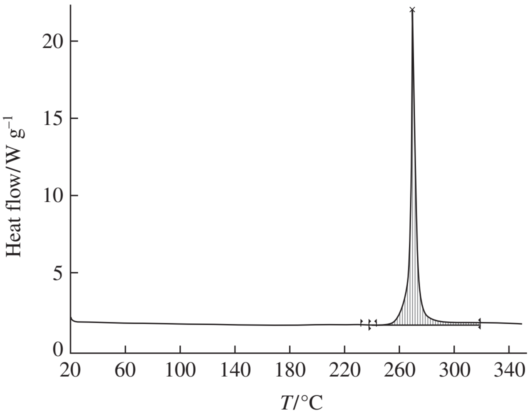


Figure 1 DSC profile of homo-PAN.

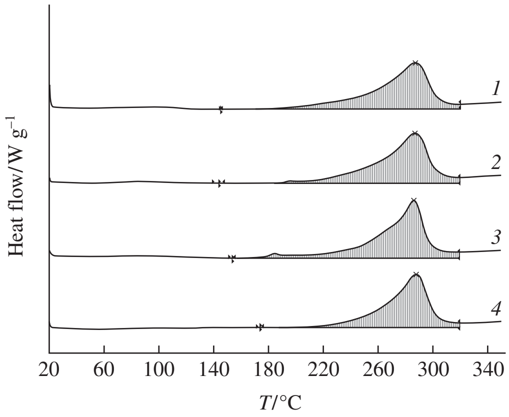


Figure 2 DSC profiles of acrylonitrile copolymers with MA and (*1*) **1**, (*2*) **2**, (*3*) **3** and (*4*) **4**.

acid was somewhat lower than the yield of copolymers with itaconates **2**–**4**. It is interesting that the homopolymer obtained under the same conditions was almost identical to copolymers with **2**–**4** in terms of molecular-weight characteristics and yields.

Figures 1 and 2 show the DSC profiles of homo-PAN and the copolymers of acrylonitrile with MA and itaconic acid **1** or its derivatives **2**–**4**, respectively. Table 2 summarizes the comparative characteristics of the DSC profiles.[§]

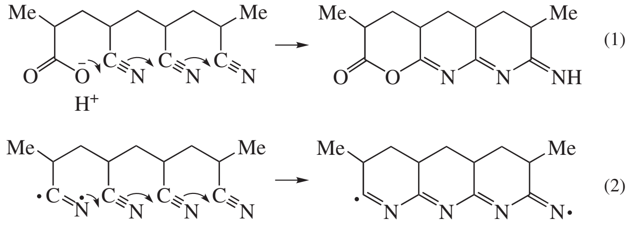
It is well known that the DSC profiles of both homo-PAN and an acrylonitrile copolymer with MA are narrow peaks.[2] It is evident that the introduction of itaconic acid **1** and its derivatives **2**–**4** leads to the broadening of the heat release peak, and the above comonomers exhibited comparable effects (Figures 1 and 2, Table 2). The start of the exothermic peaks of terpolymer is moved to the low temperature region, while the end, to the high temperature region. Obviously, the cyclization reaction enthalpies ΔH of homo- and terpolymers are about the same because the comonomer content is small, and the compositions of polymers are approximately identical (Figures 1 and 2, Table 2).

Table 2 Characteristics of the DSC profiles of acrylonitrile homo- and copolymers with MA and **1**–**4**.

Comonomer	Start of effect/°C	Peak temperature/°C	End of effect/°C	ΔH/J g^{-1}
–[a]	241.6	272.8	299.1	1185.9
1	144.3	286.9	319.7	1176.2
2	143.0	287.5	320.6	1193.0
3	153.2	286.1	319.3	1211.5
4	173.1	288.1	321.3	1136.3

[a] Homo-PAN.

The heat release peak was broadened due to the fact that compounds **1**–**4** decrease the activation energy of the cyclization of nitrile groups, and the reaction mechanism changed from radical to ion one (Scheme 1).[1,11,12] Since the amide group also initiates the process of cyclization,[4] and itaconic acid contains two carboxyl groups, exothermic effects come into play at a lower temperature for itaconic acid and compound **2**. DSC profiles (Figure 2, curves *2*–*4*) exhibit a weakly pronounced maximum at 270 °C, which was not observed in the case of a copolymer with itaconic acid; this fact suggests the more uniform introduction of itaconic acid into the copolymer.



Scheme 1 Cyclization of the nitrile groups of PAN *via* (1) ion and (2) radical mechanisms.

Thus, based on the experimental DSC data, we can conclude that the introduction of itaconic acid **1** and its mono derivatives **2**–**4**, which contain carboxyl groups, into the PAN copolymer leads to the broadening of an exothermic peak, and these comonomers exert comparable effects on the heat release peaks of the copolymers.

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Synthesis of copolymers. A magnetic anchor, 9.3 ml of DMSO, 3.0 ml (0.046 mol, 97 mol%) of acrylonitrile, 86 μl of MA (9.5×10^{-4} mol, 2 mol%), 4.7×10^{-4} mol of monomer **2**, **3** or **4** (1 mol%) and 7.5 mg of AIBN were placed in a 15-ml glass ampoule. The ampoule was filled with argon and sealed. Then, the ampoule was kept at 70 °C for 6 h and opened; the resulting polymer solution was poured out into water, and the obtained polymer was filtered off.

[§] The DSC analysis was conducted on a DSC-823e instrument from Mettler Toledo in an atmosphere of N_2 at a heating rate of 5 K min^{-1}.