Journal of Thermal Analysis, Vol. 27 (1983) 307–314

INVESTIGATION OF THE THERMAL TRANSFORMATIONS OF ACRYLONITRILE COPOLYMERS WITH METHYLTHIIRANE IN DILUTE SOLUTION IN DIMETHYLFORMAMIDE

S. A. Agranova, G. A. Polotskaya, N. A. Shirokov,
V. G. Baranov and *Yu. N. Sazanov*

INSTITUTE OF MACROMOLECULAR COMPOUNDS, ACADEMY OF SCIENCES
OF THE U.S.S.R., 199004 LENINGRAD, BOLSHOY PROSPEKT 31 U.S.S.R.

(Received January 4, 1983)

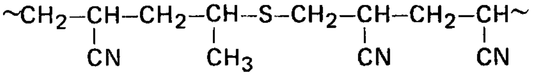
The effect of introduction of the comonomer methylthiirane (MT) into the main chain of polyacrylonitrile (PAN) on the thermal transformations of the macromolecules in dilute DMF solution was studied. For this purpose, statistical copolymers of acrylonitrile and MT were synthetized and their pyrolysis in solution was investigated. It was found that introduction of the thioether group into the main chain of PAN results in essential changes in the thermal behaviour of the copolymers as compared to the homopolymer. The results of rheological, thermal and spectral studies on the solutions suggest that the direction of the thermochemical reaction changes on introduction of the thioether group into the PAN molecule. In such copolymers the reaction will preferably proceed by the $-C{\equiv}N$ groups forming conjugated cyclic structures.

The introduction of various comonomers into the chain of the starting material polyacrylonitrile (PAN) is known to have a significant effect on the rate of formation and on the structural defects of carbon fibres prepared from the copolymer. In this process various reactions take place, resulting in the polyconjugated structure that provides the high strength, high elastic modulus and high thermal resistance of the carbon fibres. Carbon fibres have been obtained from acrylonitrile (AN) copolymers containing as comonomers methacrylate, methyl methacrylate, vinyl acetate, etc. [1]. On introduction of the comonomer, the thermal effect in thermal oxidation is lowered and this stage in the manufacture of carbon fibres is thereby facilitated.

The transformations of the homopolymer PAN during thermal processing of its dilute solutions in dimethylformamide (DMF) were investigated in [2]. The results indicated that during the thermal processing of solutions whose concentration satisfies the Debye criterium [3, 4] chemical reactions proceed preferentially intramolecularly, leading to specific changes in intrinsic viscosity $[\eta]$ and in the anisotropy of the Kuhn segment $(\alpha_1 - \alpha_2)$. If the concentration of the solution is raised, the coiled PAN macromolecules will overlap, allowing the formation of interchain contacts. This is reflected in the form of the relationships $[\eta] = f(c_{htr})$ and $(\alpha_1 - \alpha_2) = f(c_{htr})$ in heat treatment. (The subscript *htr* relates to the heat-treated samples.)

By analogy to the DTA data [5] for AN copolymers, it may be presumed that the introduction of a comonomer into the PAN macromolecules will have a fundamental effect on the reactions proceeding during the thermal treatment of these copolymers.

At present practically no information is to be found in the literature on the effect of sulfide groups on the properties of acrylonitrile copolymers. For this reason it appeared of interest to study the effect of introduction of the thioether group into the main chain of PAN on the thermal transformations of the macromolecules in dilute DMF solutions of the copolymers. For this purpose we synthetized statistical copolymers of AN with methylthiirane (MT):



$$\sim CH_2-\underset{CN}{CH}-CH_2-\underset{CH_3}{CH}-S-CH_2-\underset{CN}{CH}-CH_2-\underset{CN}{CH}\sim$$

and studied some characteristics of their pyrolysis in solution by viscosimetry, DTA and IR spectroscopy.

Experimental

The AN–MT copolymers, varying in MT content, were synthetized according to [6]. The samples for study of the changes in intrinsic viscosity, DTA curves and IR spectra due to thermal treatment of dilute solutions of the polymers were prepared as described in [2]. The viscosity of the solutions was measured in an Ubbelohde viscosimeter at 25°. Both the thermally-treated and the untreated copolymers presented a sharply expressed polyelectrolytic effect (Fig. 1). This phenomenon was found to be common for any AN copolymer in which a comonomer containing sulfur atoms was utilized. The existence of the effect is independent of the position of the sulfur atoms relative to the main chain, of the type of sulfur compound, and even of the valence of the sulfur atom in the comonomer. For instance, a concentration-dependence of the reduced specific viscosity η_{sp}/c characterizing the polyelectrolytes was observed for a copolymer of AN with 1% divinyl sulfoxide, in which the sulfur atoms are located in side-chains (Fig. 1, curve 2).

To suppress the polyelectrolyte effect, we measured the intrinsic viscosity $[\eta]$ of the copolymers in a solvent composed of 0.1 mol/m^3 LiBr in DMF. Under such conditions, the reduced specific viscosity η_{sp}/c *vs.* c relationship was linear, and $[\eta]$ was determined in the usual manner.

DTA curves were recorded with a modified MOM derivatograph. The sample mass was 5 mg, a platinum crucible was used, the heating rate was 10 deg/min, and the atmosphere was air or helium.

Infrared spectra were recorded in the range 700–4000 cm^{-1} with a UR-20 double-beam prism spectrophotometer. The samples were prepared by comparison of a dispersion of the polymer in potassium bromide.

The intensity of the ν_{CN} valence band at 2255 cm^{-1} was evaluated relative to the reference band at 1460 cm^{-1} [7].

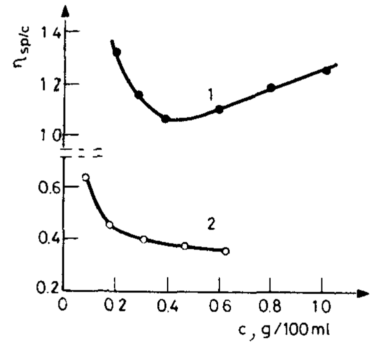


Fig. 1 Reduced specific viscosity *vs.* concentration for the copolymers AN–MT (curve 1) and AN–DVSO (curve 2)

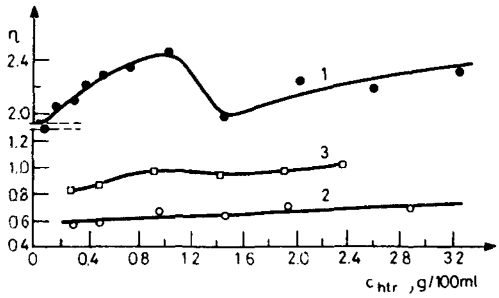


Fig. 2 Intrinsic viscosity *vs.* concentration of solutions at heat treatment. Curve 1 – PAN; curve 2 – copolymer AN–MT 92:8; curve 3 – copolymer AN–MT 97:3

Results and discussion

Using the experimental technique described in [2], we studied the effect of thermal treatment on the intrinsic viscosity of AN–MT copolymers containing different amounts of MT. Figure 2 shows the intrinsic viscosity *vs.* concentration curves for the heat-treated polymers, and also the analogous curve for the homopolymer PAN (from [2]). The character of the relationship $[\eta] = f(c_{htr})$ for the copolymers can be seen to differ significantly from that for the homopolymer.

Further studies of the direction of the thermochemical reactions taking place in the macromolecules of the homopolymer and of the copolymers were performed by DTA and IR spectroscopy.*

As reported in [8], the introduction of a second monomer into the PAN chain molecule changes the temperatures of the onset and the maximum of the thermal

---

*The authors are indebted to A. N. Krasovsky for aid in recording the IR spectra.

effect. We observed a change in the character of the DTA curves in our studies of AN–MT copolymers. These curves and the curve corresponding to the homopolymer, recorded in air, are presented in Fig. 3. The narrow exothermic peak of the homopolymer is observed at 315°. Introduction of the thioether group not only lowers the onset and maximum temperatures of the exothermic peak, but also distributes the heat liberated in a broader temperature interval, promoting pyrolysis of the copolymers without thermal shock.

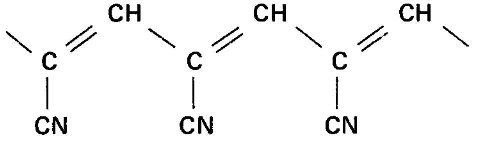
Polymers separated after the heat treatment of solutions of various concentrations in DMF were studied by DTA in helium. The relationships T_{max} *vs.* c_{htr} obtained experimentally for the homopolymer and for two copolymers differing in MT content are presented in Fig. 4. The curves demonstrate that, even at very low concentrations of the heat-treated solutions, the temperature of the peak maximum is lower than for the polymers before heat treatment (PAN: 300°, AN–MT 97:3: 288°, AN–MT 92:8: 278°). The curves show the different behaviour of the homopolymer and the copolymers. For PAN, the curve T_{max} *vs.* c_{htr} has an inflexion at the concentration corresponding to the increase in the share of intermolecular reactions; this is in conformity with the changes of $[\eta]$ (cf. Fig. 2). It is characteristic that the T_{max} values are close to constant in the sections of the curve corresponding to preferentially intramolecular and intermolecular reactions, respectively.

On introduction of a relatively high proportion (~ 8%) of thioether groups into the PAN molecule, the character of the relationship changes. When the intramolecular reactions have preference, a perceptible decrease of the temperature maximum in the DTA curve is observed, whereas subsequently, when the share of intermolecular reactions increases, T_{max} changes are insignificant. With the copolymer containing only 3% TM, the curve has an intermediate position.

Experimental data concerning the changes in the absorbance of the $-C{\equiv}N$ group are presented in Fig. 5, which demonstrates that in the case of the homopolymer the absorbance does not change, whereas in the case of the copolymer with MT a noticeable decrease (~ 15–20%) is observed in the number of $-C{\equiv}N$ groups with rising concentration of the solutions subjected to heat treatment. This decrease in the number of $-C{\equiv}N$ groups in the heat-treatment process obviously means that thermochemical reactions proceed in which these groups participate.

To summarize the findings, the following conclusions may be drawn:

(i) The nitrile groups does not participate in the thermochemical reactions proceeding in the solution of the homopolymer; the darkening of the PAN solution during heating is presumably connected with the formation of a polyene structure, the main chain containing a system of conjugated double bonds:



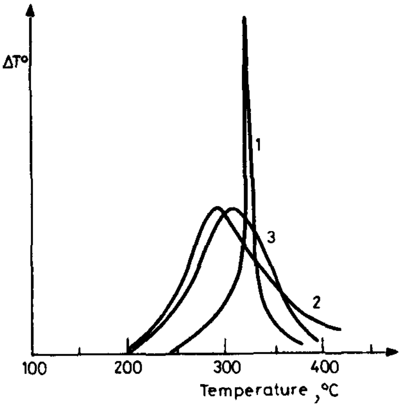


Fig. 3 DTA curves in air. 1 – PAN; 2 – copolymer AN–MT 92:8; 3 – copolymer AN–MT 97:3

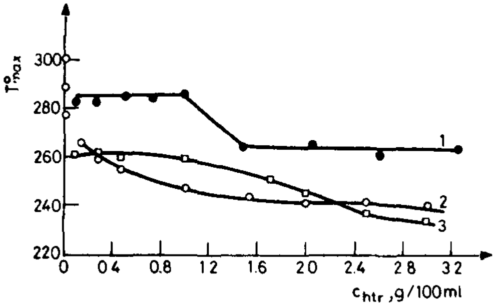


Fig. 4 Temperature maximum of the exothermic peak in helium *vs.* concentration of solutions at heat treatment. 1 – PAN; 2 – AN–MT 92:8; 3 – AN–MT 97:3

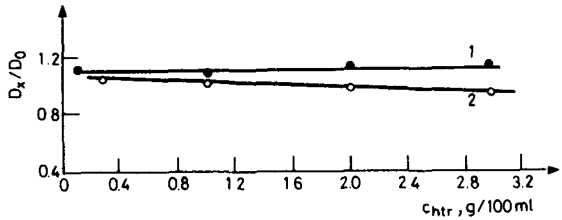


Fig. 5 Absorbance of the nitrile group *vs.* concentration of solutions at heat treatment. 1 – PAN; 2 – AN–MT 92:8

which is not in contradiction with data in the literature [9]. This conclusion is confirmed by the number of nitrile groups undergo changes during the heat treatment of PAN. When the concentration of the solution subjected to heat treatment is raised, interchain contacts are liable to be formed; this is clearly reflected in the change of the intrinsic viscosity and of the temperature of the exothermic peak.

(ii) The introduction of thioether groups into the PAN chain results in essential changes in the thermal behaviour of these polymers as compared to the homopolymer. If the results regarding intrinsic viscosity, T_{max} and the number of nitrile groups are considered jointly, it may be assumed that the introduction of thioether groups into the PAN molecule changes the direction of the thermochemical reaction. In these copolymers the reaction proceeds *via* the nitrile groups, presumably involving the formation of conjugated cyclic structures.

* * *

The authors wish to express their gratitude to Dr. G. P. Beloovskaya for her help in the discussion of the results.

Reference

1 A. A. Konkin, Carbon Fibres and Other Heat-Resistant Fibres (in Russian), Moscow, Khimiya, 1974, p. 140.

2 S. A. Agranova, B. E. Goltsin and V. G. Baranov, Vysokomol. Soed., B 23, (1981) 114.

3 P. Debye, J. Chem. Phys., 14 (1946) 636.

4 S. Ya. Frenkel, G. K. Elyashevich and Yu. N. Panov, Concentrated Solutions of Polymers (Thermodynamics and Structure). In: Advances in the Chemistry and Physics of Polymers (in Russian). Moscow, Khimiya, 1970, p. 87.

5 N. Grassie and R. McGuchan, Europ. Polym. J., 8 (1972) 257.

6 U.S.S.R. Patent No. 737411, Method for preparing copolymers of alkylene sulfides (G. A. Polotskaya, G. P. Belonovskaya and B. A. Dolgoplosk). Published in Bull. Inf., 1980, No. 20.

7 I. Dekhant, Infrared Spectroscopy of Polymers (in Russian). Moscow, Khimiya, 1976, p. 274.

8 V. Ya. Varshavsky, Composite Materials on the Basis of Carbon Fibres (in Russian). In: Itogi nauki i tekhniki, seriya Khimiya i tekhnologiya vysokomolek. soed., 8 (1976) 67.

9 A. A. Berlin, A. M. Dubinskaya and Yu. S. Moshkovsky, Vysokomol. soed., A6 (1964) 1983.

Zusammenfassung — Die Wirkung der Einführung des Methylthiiran (MT) Komonomers in die Hauptkette des Polyakrilonitrils (PAN) auf die thermischen Transformationen der Makromoleküle in einer dünnen DMF-Lösung wurde untersucht. Zu diesem Zwecke wurden statistischen Kopolymere von Akrylonitril und MT synthetisiert, und ihre Pyrolyse in Lösung untersucht. Es wurde festgestellt, dass die Einführung der Thioäthergruppe in die Hauptkette von PAN wesentliche Änderungen in dem thermischen Verhalten des kopolymers im Vergleich mit dem Homopolymer verursacht. Die Ergebnisse der rheologischen, thermischen und spektralen Untersuchungen der Lösungen suggerieren, dass sich die Richtung der thermochemischen Reaktion durch die Einführung der Thioäthergruppe in das PAN-Molekül ändert. In solchen Kopolymeren wird die Reaktion eher durch die $-C{\equiv}N$ Gruppen weitergeführt, die konjugierte, zyklische Strukturen formen.

Резюме — В работе исследовано влияние сомономера метилтиирана (МТ), введенного в основную цепь ПАН, на термические превращения макромолекул в разбавленных растворах в ДМФ. С этой целью синтезированы статистические сополимеры АН с МТ и изучены закономерности их пиролиза в растворах. Показано, что введение тиоэфирной группы в основную цепь ПАН приводит к существенным отличиям в термическом поведении таких сополимеров по сравнению с гомополимером. На основании совместного рассмотрения результатов реологического термического и спектрального исследований растворов, сделано предположение об изменении направления термохимических реакций при введении в молекулу ПАН тиоэфирной группы. В этих сополимерах реакции протекают преимущественно по $-C \equiv N$ -группам с образованием сопряженных циклических структур.