NOTE

Thermal Analysis of Acrylonitrile Copolymers Containing Methyl Acrylate

INTRODUCTION

Homopolymer and copolymer of acrylonitrile are widely used as a precursor for carbon fiber production. Since the thermal treatment of polyacrylonitrile (PAN) carried out by Shindo[1] for making carbon fibers, attention has been focused on the thermal properties of PAN-based polymers. They are well known to undergo structural changes due to nitrile group oligomerization during heating to yield stabilized structures.[2,3] An exothermic peak on the DSC thermogram resulted from this nitrile group oligomerization. The exotherm occurs at about 200–300°C, depending on the comonomer composition and molecular weight of the precursor polymer and polymerization method.[2,4-7] The initiation temperature of the exothermic reaction should be low and the stabilization reaction should be slow, since the heat evolved during the exothermic stabilization process may lead to low carbon yield.[8] Lower initiation temperatures also result in reduced entropic relaxation of the molecules, which translate into improved tensile properties of the resulting carbon fiber.[9]

Thermal analysis of acrylonitrile copolymers containing various comonomers has been investigated by Grassie and McGuchan.[5,6] Coleman and Sivy[10-14] conducted research on thermal degradation of acrylonitrile copolymers utilizing FTIR spectroscopy. Most of the previous work have been confined to acrylonitrile copolymers collected from polymerization of low yields in order to facilitate the theoretical investigation. But for an industrial setup, conversion has to be reasonably high from the economic point of view. The present study deals with the thermal behavior of PAN homopolymers and acrylonitrile/methyl acrylate (AN/MA) copolymers obtained from a 40 L pilot scale reactor with various comonomer compositions and polymerization yields. It was aimed at providing information on selecting parameters of the oxidation process for making carbon fibers based on AN/MA copolymers.

EXPERIMENTAL

The PAN homopolymers and copolymers used in this study were produced by solution polymerization in dimethyl sulfoxide at 60°C under nitrogen with 2,2′-azobisisobutyronitrile as the initiator. Comonomer contents in the range 0–15% were considered most desirable for the purpose of this study. Samples were withdrawn from the reactor at various reaction intervals. The polymers were recovered by precipitation of the solution in excess methanol and dried to a constant weight in a vacuum oven at 60°C.

The average molecular weight and polydispersity ($\bar{M}_w/\bar{M}_n$) of various PAN homopolymers and copolymers were determined by a Waters Model 440 gel permeation chromatograph (solvent: dimethylformamide containing 0.5 wt % of LiBr; column: μ-Bondagel E-Linear) and are shown in Table I. Also listed are the compositions of the AN/MA copolymers that were determined by elemental analysis using a Carlo Erba elemental analyzer.

Thermograms of PAN homopolymers and copolymers were obtained using a Perkin-Elmer system 7/4 differential scanning calorimeter. Samples were heated under air purge at a heating rate of 20°C/min.

RESULTS AND DISCUSSION

Polymerization Behavior

Table I shows the characteristics of the PAN homopolymers and copolymers. The percentage conversion vs. reaction time data clearly indicate that the rate of polymerization is higher for systems of higher AN contents. The compositions of AN/MA in the copolymers are approximately the same as those in the feed. This is in agreement with the result of Grassie and McGuchan.[6] The above composition relationship does not show any significant change with respect to reaction time, as shown in Table I.
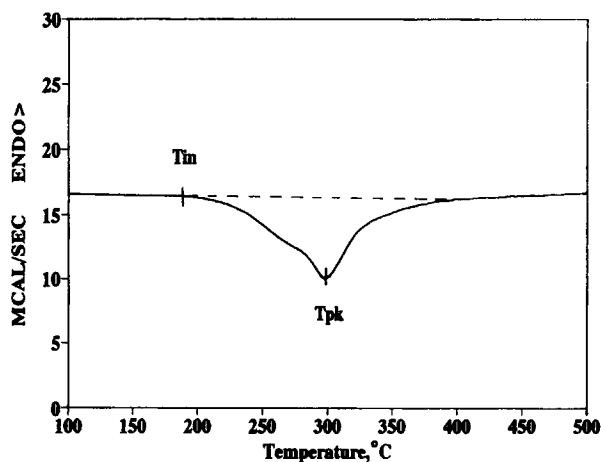
The system containing 15% MA in the feed (P85A-P85E in Table I) that is restricted to low conversions in the time frame of this study shows no significant variation of average molecular weight and dispersity with reaction time (or conversion). Others show a decrease of average molecular weight and an increase of dispersity with increasing reaction time. For vinyl polymers, the polymer made throughout the reaction has the same average molecular weight if the reaction is restricted to low conversion. However, as polymerization proceeds to higher conversions, the above relationship no longer holds, and the degree of polymerization of the polymer being formed decreases throughout the reaction as the concentration of monomer decreases.[15] Other factors, such as inefficiency in the removal of the heat of polymerization due to increased system viscosity at high conversions, may also result in local fluctuation of the reaction temperature and lead to a decrease of polymer molecular weight.

Table I Preparation of Polymers

Sample No.	Feed Composition AN/MA (Mol %)	Reaction Time (h)	Copolymer Composition AN/MA (Mol %)	Conversion (%)	$\bar{M}_w$ ($\times 10^5$)	Dispersity
P85A	85/15	1.5	86.6/13.4	17.8	6.78	3.4
P85B	85/15	2.0	85.9/14.1	23.4	6.51	3.9
P85C	85/15	2.5	86.3/13.7	30.2	7.06	3.7
P85D	85/15	3.0	85.5/14.5	39.0	7.00	3.5
P85E	85/15	3.5	86.2/13.8	46.1	6.91	3.7
P90A	90/10	1.5	91.6/8.4	19.0	6.62	4.1
P90B	90/10	2.0	89.8/10.2	27.7	6.49	4.0
P90C	90/10	2.5	89.7/10.3	37.5	6.51	4.5
P90D	90/10	3.0	91.6/8.4	54.9	5.48	4.5
P90E	90/10	3.5	90.7/9.3	70.9	5.16	5.1
P95A	95/5	1.5	95.6/4.4	20.7	7.09	3.6
P95B	95/5	2.0	96.1/3.9	27.7	6.71	4.4
P95C	95/5	2.5	95.6/4.4	42.6	6.32	4.5
P95D	95/5	3.0	96.0/4.0	59.5	5.63	4.7
P95E	95/5	3.5	95.7/4.3	76.7	5.33	5.2
P98A	98/2	1.5	97.8/2.2	23.3	7.51	3.8
P98B	98/2	2.0	98.3/1.7	34.1	6.80	4.5
P98C	98/2	2.5	98.6/1.4	46.9	6.43	5.6
P98D	98/2	3.0	98.4/1.6	60.8	6.14	5.9
P98E	98/2	3.5	97.9/2.1	79.9	5.52	6.4
P100A	100/0	1.5	100/0	26.5	7.83	3.4
P100B	100/0	2.0	100/0	39.8	6.21	4.1
P100C	100/0	2.5	100/0	67.5	5.86	5.9
P100D	100/0	3.0	100/0	81.9	5.62	6.3
P100E	100/0	3.5	100/0	91.2	4.99	6.6

Thermal Behavior

The thermal behavior of PAN homopolymers and copolymers can be obtained from the DSC thermograms of PAN. A typical DSC thermogram is shown in Figure 1.

The DSC exotherms are defined by T_{in}, the initiation temperature of the exotherm obtained from the intersection of the base line and the left-hand side of the exothermic peak, and T_{pk}, the exothermic peak temperature. The T_{pk} and T_{in} data for PAN homopolymers and copol-

Figure 1 Typical DSC thermogram of PAN.
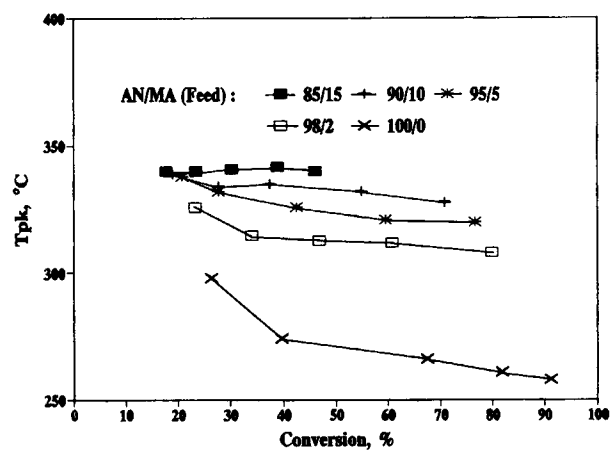
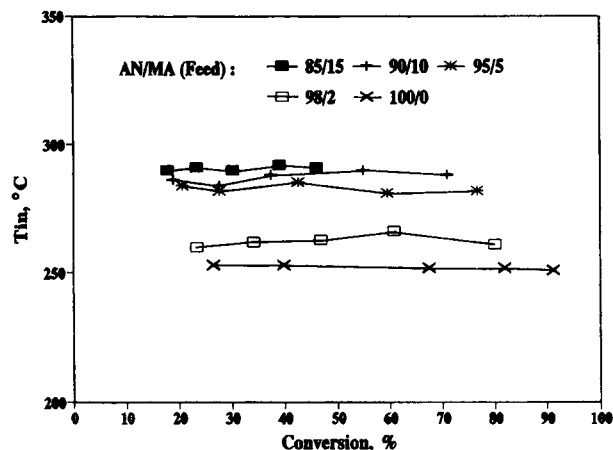**Figure 2** Exothermic peak temperature of PAN homopolymers and AN/MA copolymers.

Figure 3 Initiation temperature of the exotherm of PAN homopolymers and AN/MA copolymers.

ymers in Table I plotted against the conversions for respective samples are shown in Figures 2 and 3. Figure 2 indicates that T_{pk} decreases with increasing comonomer content of AN in the feed. For homopolymers and copolymers with the same comonomer compositions, T_{pk} decreases with increasing polymerization conversion (or yield). It is also observed in Figure 2 that the extent of decrease of T_{pk} is greater for systems of higher AN content. The exothermic peak temperature for the copolymers containing 15% MA in the feed is relatively insensitive to the yield of polymerization. This polymerization yield dependence of T_{pk} is similar to that of the average molecular weight of the homopolymers and copolymers described earlier. Previously reported data by other authors[4,7,16] indicate that T_{pk} decreases with decreasing molecular weight. Thus, it is believed that the decrease of T_{pk} with respect to increasing polymerization yield in this study is due to the decrease of polymer molecular weight as the polymerization proceeds to higher conversions. A somewhat different behavior was observed for T_{in} in Figure 3. The initiation temperature of the exotherm, although it decreases with increasing comonomer content of AN as shown in Figure 3, does not show any polymerization yield dependence as does the T_{pk}. This indicates that T_{in} is a function of comonomer composition and does not change with polymer molecular weight or polymerization yield.

CONCLUSIONS

Polymerization experiments for PAN homopolymers and AN/MA copolymers of various comonomer compositions and polymerization yields indicate that the rate of polymerization is higher for systems of higher AN content. The composition of comonomers in the polymer is approximately the same as that in the feed and does not show any significant change with respect to reaction time

(or yield). Except for the system containing 15% MA in the feed that is restricted to low conversions, the average molecular weight decreases and the dispersity increases with increasing reaction time.

From the DSC studies of PAN homopolymers and AN/MA copolymers, it is concluded that the exothermic peak temperature (T_{pk}) is a function of comonomer composition and polymerization yield. The initiation temperature of the exotherm, however, is only a function of comonomer composition and does not change with polymerization yield.

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