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Effect of the comonomer addition sequence in the synthesis of an acrylonitrile terpolymer on the solution rheology and fiber properties

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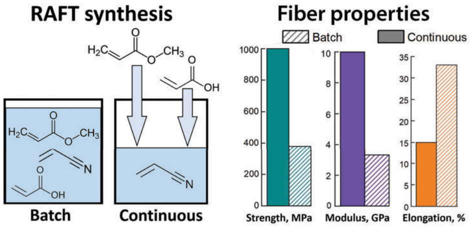
Polyacrylonitrile terpolymers based on acrylonitrile, acrylic acid, and methyl acrylate were synthesized by reversible addition–fragmentation chain-transfer polymerization with varying the monomer addition sequence during the synthesis. The monomer introduction sequence in the synthesis of a ternary copolymer significantly affects both the rheological properties of solutions and the strength of obtained fibers.



Keywords: polyacrylonitrile, reversible addition–fragmentation chain-transfer polymerization, comonomer sequence, rheology, fiber spinning.

Polyacrylonitrile (PAN) is the main precursor for high-strength carbon fibers production.[1] Various methods have been developed for the synthesis of PAN copolymers with various comonomer compositions and properties.[2,3]

Both binary and ternary PAN copolymers are used as carbon fiber precursors. The former are obtained by polymerization of acrylonitrile (AN) with alkyl acrylates or acid comonomers such as acrylic acid (AA) and itaconic acid.[2,4] Ternary PAN copolymers contain both types of monomers. Methyl acrylate (MA) is traditionally used as alkyl acrylate.[2,4,5] It is introduced into the copolymer as an inert comonomer from the viewpoint of subsequent radical cyclization[6] because MA increases chain flexibility and reduces nitrile–nitrile interactions in the polymer.[7]

Reversible addition–fragmentation chain-transfer (RAFT) polymerization makes it possible to control the sequence of monomer units along a chain, which has a significant effect on the polymer properties.[8,9] The optimal methods of synthesis and component addition are extremely important for obtaining high-quality PAN fibers, especially, precursors of high-strength carbon fibers.[10]

Previously, binary copolymers of AN and AA[11] and ternary AN–AA–MA[12] copolymers were studied. These studies showed that the synthesis method (classical or RAFT polymerization) and the method of introducing comonomers into the reaction medium (batch, continuous, and semibatch) affected the rheological and thermal properties of copolymers.

In this work, we obtained two series of AN/MA/AA ternary copolymers by RAFT polymerization. First, the synthesis was carried out with the continuous introduction of AA and MA into the reaction mixture containing AN, an initiator, and a RAFT agent to obtain a polymer with a predominantly block-random distribution of PAN-*block*-P(AN-*co*-MA-*co*-AA) units (PAN1 sample). Second, all monomers were added to the reaction mixture at the same time, which led to the formation of a copolymer with a more uniform unit distribution along the chain (PAN2 sample).[13] Dimethyl sulfoxide was used as a solvent.

The polymers were characterized by size-exclusion chromatography and capillary viscometry according to ASTM D2857-16.[14] Table 1 summarizes monomer sequence distributions, dispersity in terms of molecular weight $Đ$, the rheological properties of solutions, and the mechanical properties of fibers.

Figure 1 shows (*a*) the concentration dependence of the reduced viscosity of the samples and (*b*) the dependence of the specific viscosity on $c[\eta]$, which reflects the volume occupied by macromolecules in solution.

The intrinsic viscosities of the PAN1 and PAN2 samples were the same, while PAN1 was characterized by a large slope of the concentration dependence of the reduced viscosity, *i.e.*, a higher Huggins constant, which indicates a worse affinity for the solvent compared to that of PAN2. However, differences in the behavior of dilute solutions disappeared if the parameter $c[\eta]$[15] was used [Figure 1(*b*)]. Due to the slight deviation of PAN2 solution in the

Table 1 Characteristics of the synthesized copolymers.

Sample	AN/MA/AA (mol%)	M_n/kg mol^{-1}	M_w/kg mol^{-1}	$Đ$	$[\eta]$/dl g^{-1})	k_H	Addition of AA and MA
PAN1	88.2/9.8/2.0	72.6	110	1.51	1.8 ± 0.01	0.46 ± 0.05	Continuous
PAN2	89.7/6.8/3.5	75.9	105	1.38	1.8 ± 0.03	0.39 ± 0.08	Batch

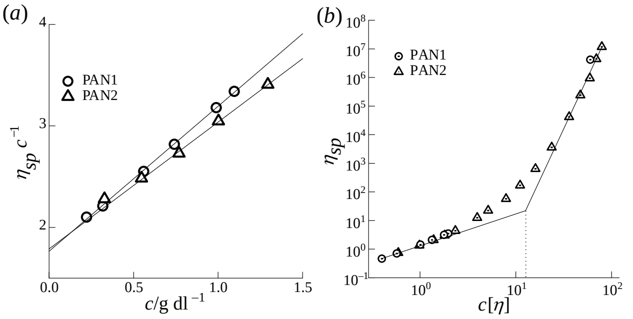


Figure 1 (*a*) Concentration dependence of the reduced viscosity and (*b*) specific viscosity as a function of $c[\eta]$.

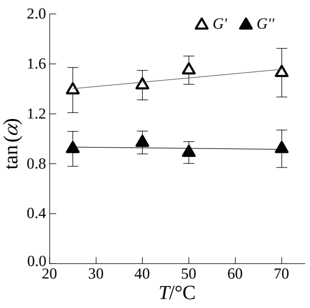


Figure 3 The temperature dependences of the slopes of frequency moduli in the terminal zone for a 30% PAN2 solution.

region of high concentrations, we assumed a similar behavior. For concentrations to ~0.5%, a linear dependence in the log–log coordinates with a slope of 1 was observed.[15] The second linear region with a slope of 7 described the behavior of concentrated solutions. According to Ebagninin *et al.*,[15] the bending point of the specific viscosity curve was used to determine a crossover concentration of ~7% for both copolymers, which corresponds to a transition to the region of formation of an entanglement network in semidilute solutions.

The rheological behavior of concentrated solutions was investigated for these samples. Figure 2 shows the flow curves and the frequency dependences of loss and storage moduli for a 30% PAN2 solution at various temperatures.

The highest Newtonian viscosity values decreased with temperature and the corresponding plateau to the region of high shear rates widened [Figure 2(*a*)]. The activation energy of the solution viscous flow was higher than that for binary copolymers of a similar molecular weight: 37 kJ mol^{-1} compared to 26 kJ mol^{-1}.[11] Figure 2(*b*) shows that, as the temperature was from 25 to 70 °C, the storage modulus decreased monotonically, and the second crossover point corresponding to the predominance of elastic forces over viscous ones shifted to the region of higher strain frequencies from 30 to 200 rad s^{-1}.

Interestingly, the slopes of the frequency dependences in the terminal zone, which characterize the relaxation properties of macromolecules, remained unchanged as the temperature was increased. The slopes of 1.4 and 0.9 found for the elastic modulus and the loss modulus, respectively, in the test polymer solutions (Figure 3) differed from the predicted values of 2.0 and 1.0 based on a standard viscoelastic Maxwell model in the linear zone.

Figure 4 compares the viscoelastic properties of the solutions of PAN1 and PAN2. A transition to the region of concentrated solutions was combined with the appearance of a significant difference in the rheological behaviors of copolymers with different component loading sequences. The highest Newtonian viscosity plateau of solution with the continuous loading of AA and MA (PAN1) was significantly narrowed down to 0.1 s^{-1}. The viscosity in this shear rate range for the PAN1 solution was higher by a factor of 4.5 (at comparable concentrations) that that of a PAN2 copolymer solution obtained with batch component addition.

The comparison of viscoelastic properties showed that the PAN1 solution had higher moduli and lower values of tan(α) in the terminal zone, which indicates a higher structuring of that system compared to PAN2. This behavior can be explained by a decrease in the solvent affinity for the polymer and, accordingly, by greater polymer–polymer interactions upon transition to the region of concentrated solutions.

Figure 5 shows the flow curves of concentrated solutions at different temperatures and polymer concentrations. A 35% solution of PAN2 at 40 and 70 °C and a 40% solution at 70 °C were significantly less viscous than a 28% solution of PAN1 at 25 °C. It was noted that they did not form a stable jet when flowing out of a capillary in the course of test spinning. The flow process itself was accompanied by periodic thinning of the jet followed by breakage due to insufficient elasticity. Therefore, a 40% solution was chosen for the subsequent comparative spinning of fibers, and spinning was carried out at 40 °C.

Fiber samples were obtained by a mechanotropic spinning method[16] on a laboratory line[11] in the regime of maximally possible orientational and plasticization drawings. A gel fiber was formed from a solution without the use of a coagulation bath due to high shear deformations in this process, at which the orientation of polymer in the outflowing jet occurred, followed by phase separation and solvent squeezing out onto the fresh fiber surface as a result of stretching. Ternary copolymers with a less uniform comonomer distribution along the chain obtained with the continuous addition of components are subject to large ratios of spunbond, orientational, and thermal stretching. As a result, fiber samples with total draw ratios of 5.3 and 4.2 were obtained from solutions of PAN1 and PAN2 copolymers, respectively. The mechanical properties of the fibers are given in Table 2.

The possibility of achieving a higher limiting draw ratio allowed us to obtain fiber samples with high mechanical properties: an average tensile strength of 1 GPa and an elastic modulus of 10 GPa, which is 2.5 times higher than that for a

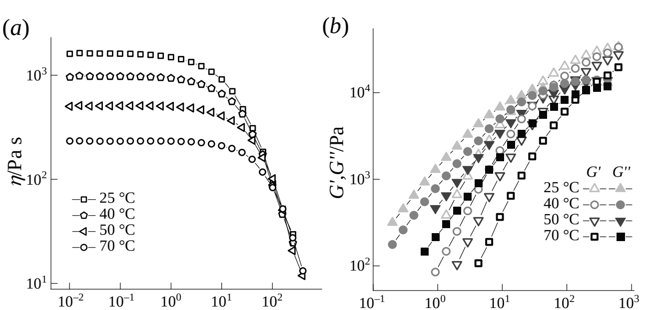


Figure 2 (*a*) Flow curves and (*b*) the frequency dependences of storage and loss moduli for a 30% PAN2 solution at different temperatures.

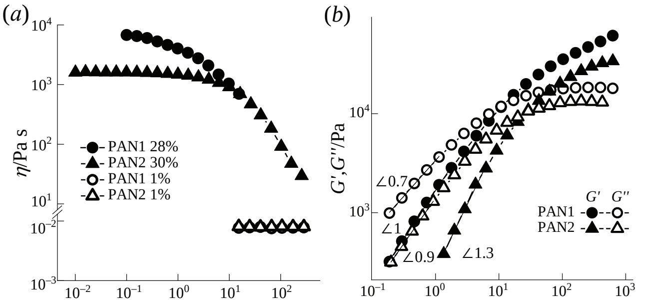


Figure 4 (*a*) Flow curves for different concentrations and (*b*) frequency dependences of 28 and 30% solutions of PAN1 and PAN2 at 25 °C. The symbol ∠ shows the values of tan(α) in the terminal region.

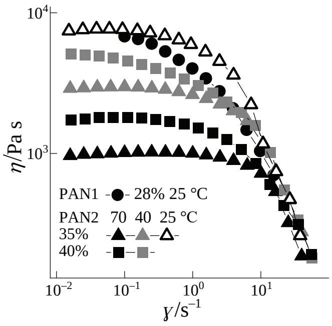


Figure 5 Flow curves of concentrated PAN1 and PAN2 solutions at various temperatures and polymer concentrations.

Table 2 Mechanical properties of polymer fibers with continuous and batch comonomer addition modes during the synthesis.

Sample	Strength/MPa	Modulus/GPa	Elongation (%)
PAN1	1000 ± 200	10 ± 1	15 ± 5
PAN2	390 ± 50	3.5 ± 0.3	34 ± 5

sample produced from a copolymer of the same molecular weight but with a regular distribution of comonomer units.

The results of this work confirmed the effect of the chain microstructure specified in the course of the RAFT synthesis. The uniform distribution of comonomers along the chain contributes to the better dissolution of the polymer, making it possible to obtain much less viscoelastic solutions in the region of concentrated solutions. In terms of fiber spinning, the better stretching ability was noted for the less regular copolymer, from which it was possible to obtain significantly stronger fibers.

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