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# Synthesis of Acid Dyeable Acrylonitrile Copolymer

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*In this paper, a unique and updated technique was applied to obtain an acid dyeable copolymer of acrylonitrile by solution polymerization of acrylonitrile, and a kind of alkaline monomer F (N,N-dialkylaminoethylacrylate). Azodiisobutyronitrile (AIBN) was used as initiator to prepare the copolymer in sodium sulfocyanate aqueous solution. The effect of initiator concentration on the polymer's molecular weight and conversion during polymerization was studied. The relation between concentration of the alkaline monomer F and the polymer conversion, as well as the relation between concentration of the alkaline monomer F and the % dye-uptake of the copolymer are discussed. The influence of pH was also researched. The structure of the copolymer was characterized by IR and NMR. The copolymer has excellent acid dyeable characteristics.*

**Keywords** acid dyeable, acrylonitrile, comonomer, solution polymerization, fiber

## Introduction

Poly(acrylonitrile) (PAN) fiber is becoming a more diversified, functional and high-performance fiber (1–3). The composite fabric of PAN fiber and natural fiber, such as wool, is applied far and wide (4). In the macromolecules of the wool there are some basic functional groups. They may be dyed by acid dyes. Whereas, nowadays most PAN are synthesized with an acid comonomer alone with the acrylonitrile, and they are dyed only by cation dyes. Thus, PAN fiber and wool cannot be dyed at the same time in the same dye bath. Therefore, the study and synthesis of quality acid dyeable PAN is significant (5). If the comonomer is alkaline, we can obtain acid dyeable PAN by the copolymerisation (6). In this paper, the copolymerisation of acrylonitrile and an alkaline acrylate F (N,N-dialkylaminoethylacrylate) was successful using solution copolymerisation in sodium sulfocyanate aqueous solution with AIBN as initiator. The solution of the copolymer can be spun, and a kind of acid dyeable acrylic fibers was obtained.

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## Experimental

### Polymerization

20 ml of acrylonitrile, 1 ml of monomer F, 0.2 ml of azodiisobutyronitrile and 100 ml sodium sulfocyanate aqueous solution (50%) were charged into a 250 ml three-necked flask equipped with a mechanical stirrer and a reflux condenser. The pH of the mixture was adjusted to 3–5. The mixture was agitated at 70°C for 2–4 h as the polymerization was carried out. The unreacted monomer was distilled by means of vacuum. Then 80 ml of water (40°C) was put into the reactor with agitation; phase separation of the copolymer solution took place. The copolymer was filtered, washed and dryed. Finally, the copolymer granules were prepared. The copolymer sodium sulfocyanate aqueous solution may be spun directly.

### Dyeing Test

0.5 g of the copolymer granules was charged into a flask in which there was 50 ml (1 g/L) acidic dye mandarin G. The mixture was heated to 110°C for an hour. The sample was filtered, washed and dried.

### Tests and Measurements

The conversion of monomer can be calculated by the method of weighing. The copolymer solution (1%) was prepared using N,N-dimethylacetamide(DMAc) as solvent at the temperature of 40°C. The flow time t of the copolymer solution was measured with a Ubbelohde viscometer. By means of the formula $M = K_1K_2t$, the molecular weight of the copolymer can be determined (Where $K_1$, $K_2$ are solvent coefficient and viscometer coefficient, respectively).

The absorbance was tested using a spectral photometer, according to the formula $A = \lg (I_0/I) = \varepsilon bC$ (Where $I_0$, I are strengths of incident light and transmitted light, $\varepsilon$ is the absorbtion coefficient and b is light path length in the solution). The absorbance A and the dye concentration C of the staining solution have a quantitative relationship. First, a series of absorbance for different dye concentrations of the staining solution was measured. A concentration-absorbance standard curve C-A diagram was drawn. The absorbance (A) of the residual dye in the solutions, after removal of the dyed copolymer was tested. Compared with the concentration–absorbance standard curve, one can get the concentration C of the staining solution. Thus, the % dye-uptake (R) of the specimen can be determined from the equation:

$$R(\%) = (1 - C/C_0) \times 100\%$$

where $C_0$ is original concentration of staining solution.

NMR spectra were recorded on a Bruker Advance 400 Spectrometer using DMAc as solvent and tetramethylsilane (TMS: $\delta = 0$) as internal reference at 30°C.

IR spectra were recorded on a Nicolet 750 Magna-IR spectrometer by the KBr method.

**Table 1**
Relation between initiator concentration $C_I$ and the monomer conversion, molecular weight

| AIBN concentration $C_I$ (%) | Conversion (%) | $M\eta$ ($\times 10^4$) |
|---|---|---|
| 0.25 | 73.1 | 76.5 |
| 0.30 | 75.5 | 61.8 |
| 0.35 | 81.5 | 50.0 |
| 0.40 | 82.7 | 47.1 |
| 0.45 | 83.2 | 39.1 |

## Results and Discussion

### *Influence of Initiator Concentration*

According to Table 1, with the increase of the amount of AIBN ($C_I$), the active centres increased and the velocity of reaction increased, which resulted in the conversion slightly rising, and the molecular weight dropping (7).

### *Influence of Monomer F Concentration*

We changed the comonomer F $C_F$ from 0.5% to 2.5% in the copolymerisation, obtaining the data in Table 2. With the increase of the monomer F concentration, $C_F$, the copolymer's conversion slightly dropped in the copolymerization, but the % dye-uptake increased. Monomer F, a kind of alkaline tertiary amine, can totally dissolve in sodium sulfocyanate aqueous solution, and thus may partly increase the hydrophilicity of the copolymer, which causes creation of an emulsion phenomenon of the copolymer. Thus, the diffusion of the monomer toward the active end groups was obstructed. That explains the decrease of the conversion. With the increase of alkaline comonomer concentration $C_F$, there were more dyeable groups in the copolymer and larger % dye-uptake. Taking % dye-uptake and conversion of the monomer into consideration, we concluded

**Table 2**
Effect of the monomer concentration $C_F$

| Comonomer concentration $C_F$ (%) | Monomer conversion (%) | % Dye-uptake (%) |
|---|---|---|
| 0 | 84.7 | 0 |
| 0.5 | 82.5 | 85.67 |
| 1.0 | 81.6 | 91.83 |
| 1.5 | 81.5 | 95.61 |
| 2.0 | 77.6 | 96.48 |
| 2.5 | 71.3 | 97.32 |

**Table 3**
Relation between pH and conversion

| pH | Conversion % |
|---|---|
| 3.0 | 22.7 |
| 3.5 | 34.4 |
| 4.0 | 82.5 |
| 4.5 | 77.8 |
| 5.0 | 45.3 |
| 5.5 | 32.1 |
| 6.0 | 20.3 |

that an alkaline monomer F concentration of 2% was best for producing appropriate polymer for fiber production.

### *Influence of pH*

The pH was varied from 3.0 to 6.0, with the conversion of the copolymer evaluated as shown in Table 3. Both the lowest and highest pH, i.e., 3.0 and 6.0, respectively, caused poor results indicating these pH are inappropriate for applying to preparation of the copolymer. According to Table 3, the best pH of polymerization seems to be the middle, i.e., about 4.0.

### *Effect of $NaHSO_3$*

Because the nitrile group in the copolymer is oxidized very easily, the copolymer may yellow in production and application (8, 9). In order to reduce the oxidation of the copolymer, a small amount of $NaHSO_3$ was used in the polymerisation. According to Table 4, with the increase of the amount of $NaHSO_3$, the whiteness of the copolymer increased. But $NaHSO_3$ is also a chain transfer agent, so the conversion and the molecular weight of the copolymer dropped (10). Because the best molecular weight of PAN for spinning is about 50000, the $NaHSO_3/AIBN = 1/10$ is the best composition.

**Table 4**
Effect of $NaHSO_3$

| $NaHSO_3$/ AIBN | White degree (%) | $M\eta$ ($\times 10^5$) | Conversion (%) |
|---|---|---|---|
| 1/6 | 87.2 | 3.61 | 70.5 |
| 1/8 | 84.6 | 4.51 | 74.8 |
| 1/10 | 83.2 | 5.04 | 80.3 |
| 1/12 | 80.3 | 6.15 | 81.0 |
| 1/14 | 78.4 | 7.85 | 82.5 |

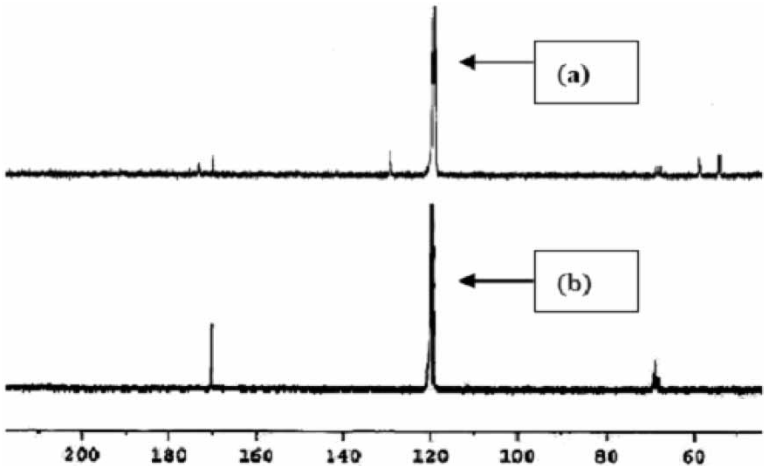

**Figure 1.** NMR spectra of the acrylonitrile homopolymer and its' copolymer.

### *Characterization of the Polymers*

In Figure 1, curve a is the NMR spectrum of the acrylonitrile homopolymer, and curve b is the NMR spectrum of the copolymer of acrylonitrile and monomer F. In both curves, a and b, there are strong peaks with chemical shift ($\delta$) 120 ppm. It is caused by the resonance type absorption peak of $^{13}$C in the $-$CN of the PAN. In curve b, there is a weak peak with chemical shift ($\delta$) 173.95 ppm caused by the resonance type absorption peak of $^{13}$C in the ester; it is absent in curve a. Thus the copolymer has many nitrile groups and a certain number of ester groups.

In the infra-red spectrum of the comopolymer of acrylonitrile and monomer F (Figure 2) the absorption peak at 2243 cm$^{-1}$ is the characteristic peak of CN in the

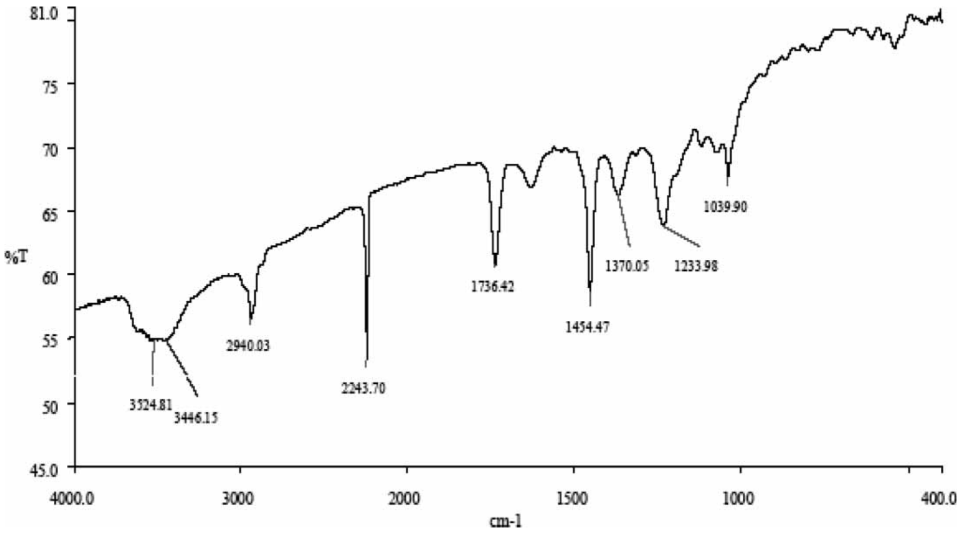

**Figure 2.** Copolymer infra-red spectra.

PAN, the peak at 1736 $cm^{-1}$ is the characteristic peak of the C=O in the ester, and the peak at 3446 $cm^{-1}$ characterizes the NH in the amine; results confirm that the product is the copolymer of acrylonitrile and monomer F.

## Conclusions

In the copolymer of acrilonitrile and monomer F, the alkaline monomer F can make the copolymer acid dyeable. With the increase of the amount of AIBN, the conversion of the copolymerization rose, and the molecular weight dropped. With increase of the monomer F concentration, % dye-uptake increased, but the monomer's conversion slightly dropped. Taking % dye-uptake, concentration of the monomer and molecular weight into consideration, $C_I = 0.35$, pH = 4.0 and $C_F = 2\%$ were optimum for the copolymerization. A small amount of $NaHSO_3$ can improve the whiteness and color stability of the copolymer and its fiber.

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