Tailoring the Swelling and Glass-Transition Temperature of Acrylonitrile/Hydroxyethyl Acrylate Copolymers

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ABSTRACT: Novel polyacrylonitrile (PAN)-*co*-poly(hydroxyethyl acrylate) (PHEA) copolymers at three different compositions (8, 12, and 16 mol % PHEA) and their homopolymers were synthesized systematically by emulsion polymerization. Their chemical structures and compositions were elucidated by Fourier transform infrared, ^{1}H-NMR, and ^{13}C-NMR spectroscopy. Intrinsic viscosity measurements revealed that the molecular weights of the copolymers were quite enough to form ductile films. The influence of the molar fraction of hydroxyethyl acrylate on the glass-transition temperature (T_g) and mechanical properties was demonstrated by differential scanning calorimetry and tensile test results, respectively. Additionally, thermogravimetric analysis of copolymers was performed to investigate the degradation mechanism. The swelling behaviors and densities of the free-standing copolymer films were also evaluated. This study showed that one can tailor the hydrogel properties, mechanical properties, and T_g's of copolymers by changing the monomer feed ratios. On the basis of our findings, PAN-*co*-PHEA copolymer films could be useful for various biomaterial applications requiring good mechanical properties, such as ophthalmic and tissue engineering and also drug and hormone delivery. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 116: 628–635, 2010

Key words: copolymerization; emulsion polymerization; films; hydrogels; hydrophilic polymers

INTRODUCTION

Acrylonitrile (AN) copolymers are one of the most important commercial materials and have much consideration in academics and industry. Appropriate techniques must be selected and polymerization conditions should be optimized to improve the quality of products when these high-performance acrylic polymers are synthesized. One of the most common methods of reaching desired properties is emulsion polymerization.[1] Faster polymerization rates, high-molecular-weight products, and a nontoxic polymerization medium are advantages of emulsion polymerization. Copolymers from emulsion polymerization have been widely used in the leather, paper, textile, paint, carpet, adhesive, and biomedical industries.[2]

The biomedical industry usually uses hydrogels that are macromolecular networks to absorb a large amount of water without dissolution.[3] Hydrogels have been extensively used as drug-delivery agents and soft-tissue substitutes. Poly(hydroxyethyl acrylate) (PHEA) is one of the most used hydrogel polymers. Because PHEA suffers from bad mechanical properties, it is beneficial to improve mechanical properties of PHEA and keep its desired hydrogel properties to use them in many applications, such as matrices for drug and human growth hormone delivery,[4] biomaterials in tissue engineering, and ophthalmic applications.[5,6] Copolymerization is one way to maintain the hydrogel properties with mechanical stability. A few studies have been reported on the copolymerization of hydroxyethyl acrylate (HEA) with various comonomers, such as styrene, butyl acrylate, and ethyl methacrylate.[7–11] On the other hand, a great deal of work has been done to develop an important industrial engineering plastic called *polyacrylonitrile* (PAN) copolymers. For example, the emulsion polymerization of AN and methyl acrylate with an acid stabilizer was largely studied by McGrath and coworkers.[12–15] However, none of the previous studies used HEA comonomer in the copolymerization of PAN to obtain copolymers with varied glass-transition temperatures (T_g's) and hydrophilicities.

In this study, we improved the synthesis and characterization of statistical copolymers of PAN–

Abbreviation	Full name	AN (g)	HEA (g)	Surfactant (g)	APS (g)	1-Dodecanthiol (g)	Water (mL)
PAN	Polyacrylonitrile	22.30	—	1.78	0.0223	0.42	42
PAN(88)-co-PHEA(12)	88 mol % PAN and 12 mol % PHEA	22.60	6.75	2.35	0.0293	0.56	44
PHEA	Poly(hydroxyethyl acrylate)	—	22.40	1.79	0.0224	0.43	43

PHEA so that we could control the hydrogel properties of HEA and use them in possible biomedical applications. There were two main objectives of this study. The first was to control the T_g's of PAN copolymers to demonstrate their processing potential. The second was to improve the mechanical stability of the HEA polymers to make them more available for biomedical applications requiring films with tailored hydrophilicities and T_g's. Attempts were also made to characterize the final copolymers structurally, thermally, and mechanically.

EXPERIMENTAL

Materials

AN (99%) and HEA (99.5%), which were obtained from Aldrich (Taukirchen, Germany) and Acros Organics (Geel, Belgium), respectively, were freshly distilled by vacuum distillation before use. Ammonium persulfate (APS; >99%) water-soluble initiator was provided from Acros Organics. 1-Dodecanthiol (Merck, Darmstadt, Germany) was used as a chain-transfer agent. DOWFAX 8390 solution surfactant was used as received. Magnesium sulfate (97% anhydrous), N,N-dimethylformamide (DMF; 99.8%), and 1-methyl-2-pyrrolidonone (NMP; 99%) were provided from Acros Organics and were used as received. Deionized water was adopted as the polymerization medium.

Homopolymer and copolymer synthesis

The copolymer synthesis was carried out in an aqueous medium via an emulsion polymerization route. A 250-mL reaction flask fitted with a condenser, glass stirrer, dropping funnel, nitrogen inlet tube, and thermocouple probe was charged with water. The temperature was raised to 65°C, and the flask was purged with nitrogen for 1 h. The surfactant, initiator (65% of total initiator), and mercaptan were added followed by the premix of the monomer mixture (20% of total monomer). The remaining monomer mixture was added over a period of 2 h. After the addition of the monomer mixture, the remaining initiator was poured through a dropping funnel. The latex was held at 65°C for an additional 30 min. The product was precipitated with a 10% aqueous MgSO₄ solution, and the copolymer was washed

with distilled water several times and then vacuum-dried at 60°C overnight. Table I shows the recipe for the polymerization of the homopolymers and copolymers. The chemical structure of the synthesized copolymer is shown in Figure 1.

Film preparation

The PAN-co-PHEA copolymer films were prepared by casting from a DMF solution having 5% polymer on a smooth glass plate under an IR lamp at about 60°C. Then, the films were vacuum-dried at 60°C for 2 h for further drying.

Characterization

The IR spectra were recorded by with a Bruker Vertex-70 Fourier transform infrared (FTIR) spectrophotometer. ^{1}H-NMR and ^{13}C-NMR spectra were obtained with a Bruker (Ettlingen, Germany) Biospin high-resolution digital 300-MHz spectrometer with hexadeuterated dimethyl sulfoxide (DMSO-d_6) as a solvent at room temperature. The intrinsic viscosity measurements were performed with an Ubbelohde viscometer (Ankara, Turkey) at 30°C in N-methyl-2-pyrrolidonone (NMP). The weight loss pattern of the copolymers and homopolymers were determined by a PerkinElmer (USA) Pyris 1 thermogravimetric analyzer (USA) under a nitrogen atmosphere with a heating rate of 10°C/min. The T_g values of the homopolymers and copolymers were evaluated with a PerkinElmer Diamond differential scanning calorimeter under a nitrogen atmosphere with a heating rate of 10°C/min. Mechanical measurements were carried out with an Instron 3367 (High Wycombe, UK) at a crosshead speed of 10 mm/min. The tensile strength and elongation length were measured
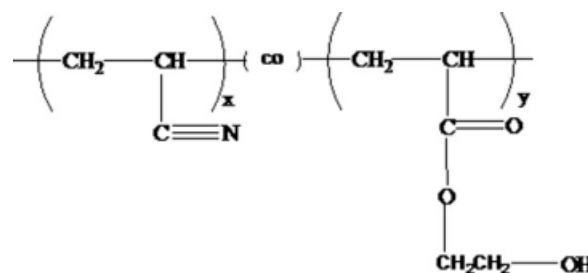

Figure 1 Chemical structure of the PAN–PHEA copolymer.

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TABLE II
Theoretical and Experimental Compositions and Intrinsic Viscosity Data for the PAN–PHEA Copolymers

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Sample (AN/HEA)	AN/HEA molar ratio				$[\eta]_{30°C}^{NMP}$ (dL/g)	T_{10} (°C)[d]
	Monomer feed	Composition[a]	Composition[b]	Composition[c]		
1	92/8	92.3/7.7	92.6/7.5	91.8/8.2	1.25	337
2	88/12	86.1/13.9	86.5/13.5	85.6/14.4	0.72	342
3	84/16	83.1/16.9	84.7/15.3	82.9/17.1	0.92	336

[a] Calculated by ^{1}H-NMR from —OCH$_2$ and —CH peaks in DMSO-d_6.
[b] Calculated by ^{1}H-NMR from —OH and —CH peaks in DMSO-d_6.
[c] Calculated by ^{1}H-NMR from —OCH$_2$ and —CH$_2$ peaks in DMSO-d_6.
[d] Temperature of 10% decomposition from TGA. $\eta_{30°C}^{NMP}$, Intrinsic Viscosity (at 30 °C in NMP Solvent) (dL/g).

during deformation at room temperature. The swelling behavior of the PHEA homopolymer and PAN–PHEA copolymers with various HEA contents were also studied. The copolymer films were immersed into water at room temperature until a swelling equilibrium was attained. The weight gain of the films was recorded as a function of time.

The equilibrium swelling ratio (SR) of the films was calculated with the following equation:

$$\text{SR (wt \%)} = \frac{W_w - W_d}{W_d} \times 100 \qquad (1)$$

where W_w is the weight of wet sample at equilibrium and W_d is the weight of the fully dried sample. The time dependency of the sorbed water was used to determine the dynamic swelling behavior of the films. The following equation was used to calculate the degree of swelling (q):

$$q = \frac{W_t}{W_0} \qquad (2)$$

where W_t is the weight of the swollen film at time t and W_0 is the weight of film at time 0.

RESULTS AND DISCUSSION

It is well known that PAN is insoluble in many solvents and degrades before it melts at about 300°C. Hence, it needs to be copolymerized with suitable monomers. In this study, we used HEA comonomer instead of traditional methyl, butyl, and ethyl acrylate. Intrinsic viscosity measurements were used to measure the relative molecular weight of these copolymers. The values of intrinsic viscosity for the copolymer series are summarized in Table II. These values were intentionally kept high to obtain ductile films. The chemical structure was elucidated by FTIR and ^{1}H-NMR and ^{13}C-NMR spectroscopy. The FTIR spectra of the copolymers and homopolymers are shown in Figure 2. The broad peak at 3442 cm^{-1} corresponded to OH stretching, whereas OH bending was seen at 1073 cm^{-1}. The aliphatic CH$_x$
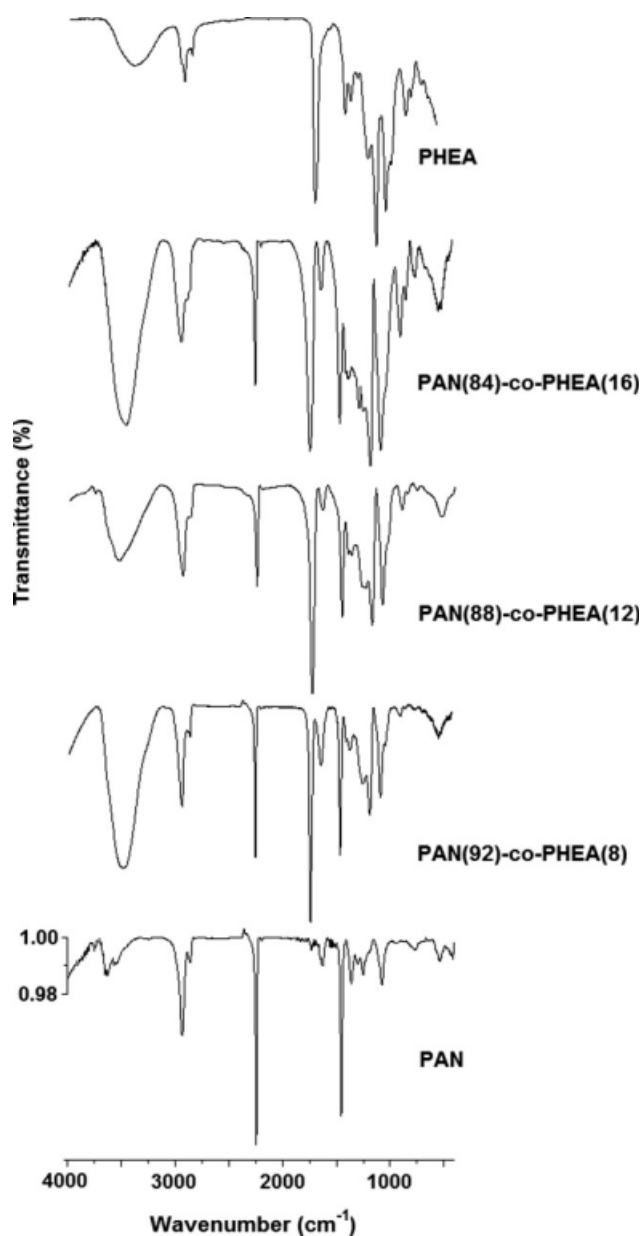
Figure 2 FTIR spectra of the copolymers and homopolymers (monomers were successfully incorporated into the chemical structure).
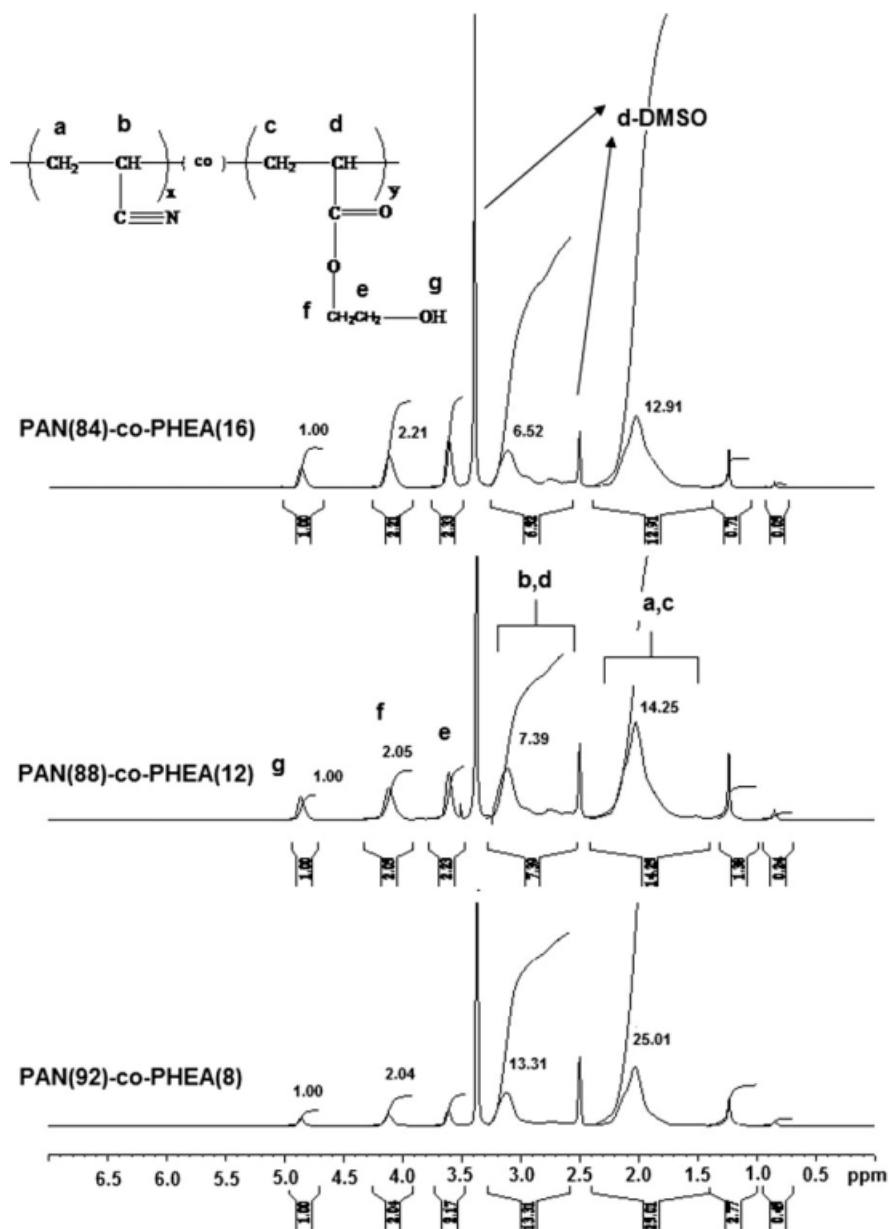
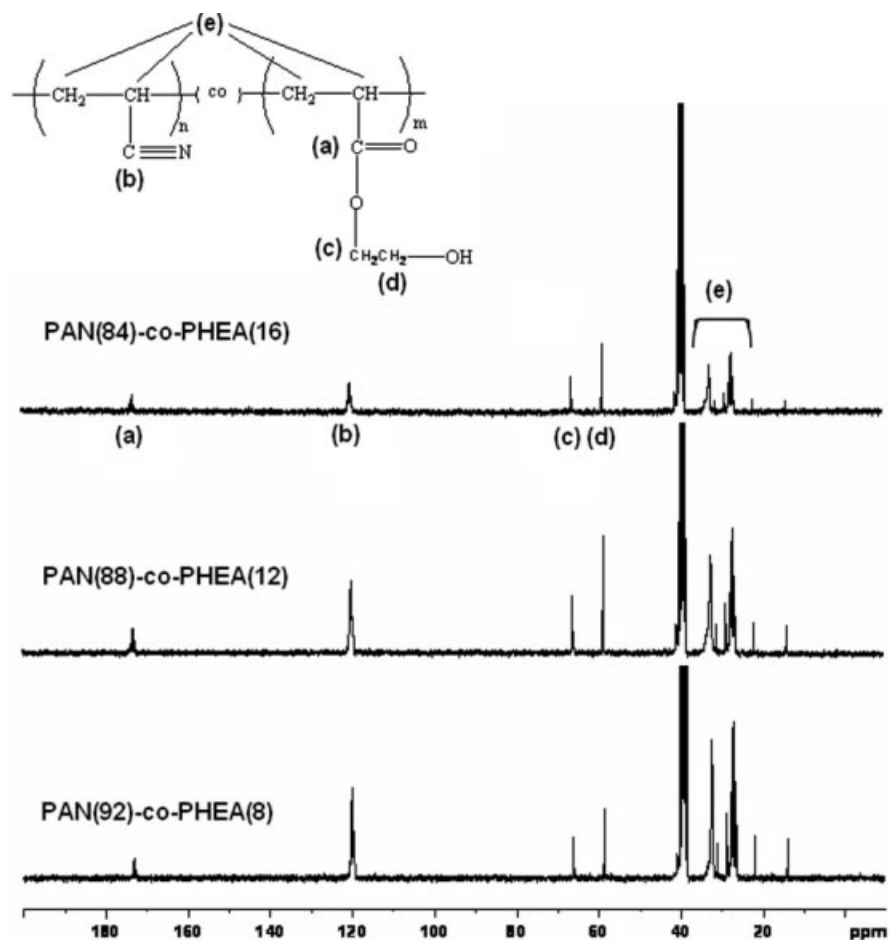**Figure 3** ^{1}H-NMR spectra of PAN–PHEA copolymers with different compositions (the chemical structure was proven by ^{1}H-NMR).

asymmetric and symmetric stretching peaks were observed at 2935 and 2864 cm^{-1}, respectively. The strong band at 1443 cm^{-1} corresponded to CH$_x$ bending. The characteristic —C≡N stretching peak was seen at 2245 cm^{-1}, and —C=O stretching was seen at 1731 cm^{-1}. The peaks between 1359 and 1078 cm^{-1} were assigned to C—C—O and O—C—C ester stretching vibrations. The chemical structures of the copolymers were confirmed by FTIR study. Also, the band intensity ratios of carbonyl to nitrile increased in the following order: PAN(92)-co-PHEA(8) to PAN(88)-co-PHEA(12) and PAN(84)-co-PHEA(16).

Figure 3 shows the ^{1}H-NMR spectra of random PAN–PHEA copolymers at various molar ratios. The resonance at 4.99 ppm was for the —OH of the hydroxyethyl group [Fig. 3(g)]. The signals at 4.11 and 3.61 ppm were assigned to —CH$_2$ protons of the hydroxyethyl group [Fig. 3(f) and 3(e), respectively]. The —CH backbone protons of the hydroxyethyl and AN groups ranged between 3.25 and 2.6 ppm [Fig. 3(b) and 3(d), respectively], and —CH$_2$ backbone protons appeared between 2.4 and 1.37 ppm [Fig. 3(a) and 3(c), respectively].

The copolymer composition was calculated with the following peaks:

1. —OCH$_2$ [Fig. 3(f)] and —CH [Fig. 3(b,d)] protons.

Figure 4 ^{13}C-NMR spectra of PAN–PHEA copolymers with different compositions. The theoretical and actual compositions are shown to be comparable.

2. —OH [Fig. 3(g)] and —CH [Fig. 3(b,d)] protons.
3. —OCH$_2$ [Fig. 3(f)] and —CH$_2$ [Fig. 3(a,c)] protons.

The theoretical and actual compositions calculated from the ^{1}H-NMR are summarized in the following equations, and the results are tabulated in Table II:

$$\text{Molar percentage of HEA} = \frac{I_{(f)}/2}{I_{(b,d)}} \times 100 \quad (3)$$

$$\text{Molar percentage of HEA} = \frac{I_{(g)}}{I_{(b,d)}} \times 100 \quad (4)$$

$$\text{Molar percentage of HEA} = \frac{I_{(f)}/2}{I_{(a,c)}/2} \times 100 \quad (5)$$

The ^{13}C-NMR spectra (Fig. 4) revealed that the characteristic signals of —C=O and C≡N appeared at 173.4 [Fig. 4(a)] and 120.4 [Fig. 4(b)] ppm, respectively. Similarly, —OCH$_2$, CH$_2$—OH, —CH$_2$, and —CH were detected at 66.3, 58.7, 32.6, and 22.07

ppm, respectively. The ^{13}C-NMR data showed that the HEA comonomer was reasonably incorporated into the copolymer structure.
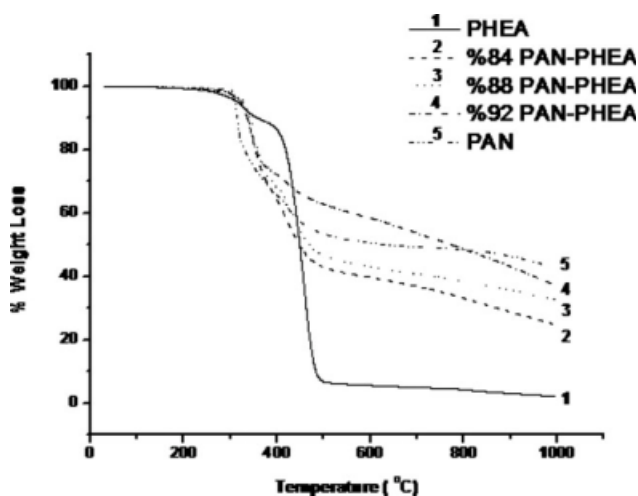
The T_g's of the copolymers were determined by differential scanning calorimetry (DSC). A typical T_g trace is shown in Figure 5. T_g values of the copolymers of PAN and polyacrylates have been reported in many studies.[16–18] However, none of the previous reports have ever issued the T_g of the PAN–PHEA copolymer. The T_g of the copolymers was between those of the homopolymers of PHEA (T_g = 3.5°C) and PAN (T_g = 104°C). As expected, the T_g values decreased with increasing molar fraction of hydrophilic comonomer addition of HEA. Additionally, the DSC thermograms of the copolymers showed that they did not decompose up to 240°C.

Thermal analysis of the homopolymers and copolymers was carried out to determine the degradation temperature and also the weight loss behavior during successive heating over a period of time. The study showed that the thermal characteristics were affected by the weight percentage of the comonomer, as observed earlier for comparable
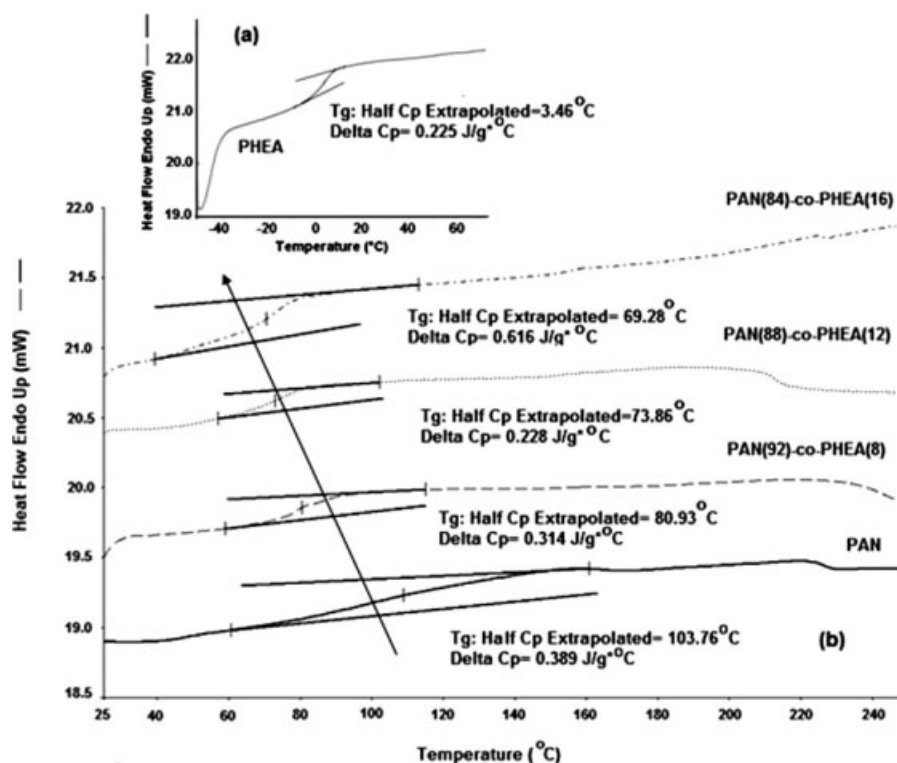
Figure 5 DSC thermograms of (a) PHEA and (b) the PAN homopolymer and copolymers. T_g of PAN was successfully lowered from about 104 to 70°C (heating rate = 10°C/min, nitrogen atmosphere). Cp, heat capacity at constant pressure.

systems.[13,16,19,20] The thermogravimetric analysis (TGA) thermograms of the synthesized copolymers and homopolymers are shown in Figure 6. There were two degradation steps for pure PAN, namely, cyclization and aromatization of the polymer by the release of HCN.[21,22] Similarly, a two-step degradation is commonly observed for the copolymers. This can possibly be due to the side-group degradation followed by the main-chain degradation. TGA also

revealed that copolymer series were thermooxidatively stable up to 330°C, which is high enough for many applications.[10,11,15]

For mechanical tests, three samples for all of the compositions were prepared, and all samples were subjected to a progressively increasing tensile force until they fractured. The averages of the elastic modulus (E), ultimate tensile strength (UTS), and elongation at break (EAB) for these three samples for different compositions of PAN–PHEA copolymer films are given in Table III. As expected, the E values of the films decreased with increasing HEA content because the polymer structure became softer and the polymer chains started to flow under the load with the addition of HEA. The maximum E value, which was 7.85 MPa, was obtained for films containing 92% PAN. Similarly, a decrease in the AN unit in the copolymer decreased the UTS values. As the AN content decreased from 92 to 84%, the UTS values decreased from 29.65 to 12.84 MPa. On

Figure 6 Weight-loss temperatures for the homopolymers and copolymers. The copolymers were thermooxidatively stable.

TABLE III
Mechanical Properties of the PAN–PHEA
Copolymer Films

Sample	UTS (MPa)	E (MPa)	EAB (%)
PAN(92)–PHEA(8)	29.65 ± 0.50	7.85 ± 0.88	52.89 ± 1.40
PAN(88)–PHEA(12)	22.03 ± 1.41	1.94 ± 0.13	428.45 ± 45.65
PAN(84)–PHEA(16)	12.84 ± 0.21	1.61 ± 0.25	337.17 ± 26.45

the other hand, EAB increased with increasing HEA content from 8 to 12%. When the HEA content was increased further, in addition to the decrease in E and UTS, a decrease in EAB was obtained. This indicated a relative loss in the mechanical durability of the films compared to the films having 8–12% HEA. The PAN(88)–PHEA(12) sample showed the highest EAB value with 428.45%. As a result, it was possible to conclude that the mechanical properties of these films was tailored with the addition of HEA. Also, these films could be used in biomedical applications, such as ophthalmic applications and wound recovery requiring mechanical stability to handle frictional stresses formed during operations.[5,6,23]

Swelling behavior analysis of polymer matrices is especially important for the design of controlled-release devices. It is possible to predict the drug-release rate by determination of the dynamic swelling properties of the polymer matrices.[24] In this study, SR and q of the PAN–PHEA copolymers having various PAN contents were determined. Table IV represents the SRs and densities of solution-cast copolymers at various HEA percentage loadings. As expected, the homopolymers of HEA absorbed tremendous amount of water because of its hydrogel properties. The swelling ratio of the copolymers decreased with decreasing HEA content. Also, an increase in the HEA content lowered the density of the copolymers. This may have been correlated to the decrease in T_g with increasing HEA content.
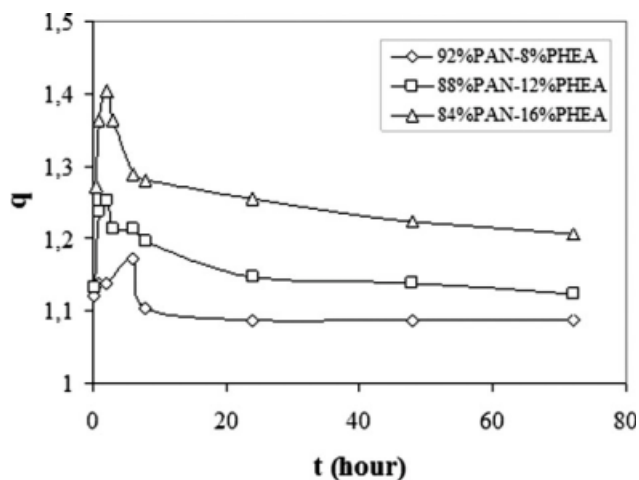
The variation of q with HEA content in the copolymer is shown in Figure 7. As expected, q decreased with decreasing HEA content. Moreover, q reached a maximum in 1–6 h. Then, a decrease in q was observed. Finally, the q values stabilized. This effect is called the *overshooting phenomenon*.[25] Basically, this phenomenon could be attributed polymer relaxation. The diffusion of the solvent into the hydrogel part (HEA) of the copolymer was faster than that into the AN chain. Therefore, more water was initially absorbed. Then, when the copolymer relaxed to equilibrium conformation, the films expelled some water.

Figure 7 q versus t for various PAN–PHEA copolymers.

successfully synthesized by emulsion polymerization. FTIR, ^{1}H-NMR, and ^{13}C-NMR spectroscopy conformed the chemical structures of the copolymers. The DSC study revealed that the T_g's of the copolymers varied between the T_g's of the homopolymers of PAN and PHEA. Additionally, the T_g's of PAN were lowered from 104 to 69°C with the addition of the comonomer. All of the PAN–PHEA copolymer compositions resulted in mechanically stable, free-standing films. UTS and E of the films decreased with increasing HEA content. The overshooting effect was observed for the swelling behavior of the PAN–PHEA copolymers. The q values of the all of the copolymers presented here increased up to a critical time. After a certain time, the q values decreased and reached equilibrium because of the relaxation phenomenon of the polymer network. Moreover, q increased with increasing HEA content. As a result, these films could be used in biomedical research requiring mechanically stable films with controllable hydrophilicities and T_g's.

CONCLUSIONS

Thermooxidatively and mechanically stable PAN-*co*-PHEA random copolymers and homopolymers were

TABLE IV
SRs and Densities of the Copolymers with Various HEA Loadings

HEA content (%)	SR (%)	Density (g/cm^3)
8	7.94	1.15
12	10.31	1.11
16	21.82	1.06
100	1065	Not applicable

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