Preparation and Characterization of Acrylonitrile-Ethyl Methacrylate Copolymers and the Effect of LiClO$_4$ Salt on Electrical Properties of Copolymer Films

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ABSTRACT: Copolymers of poly(acrylonitrile-*co*-ethyl methacrylate), P(AN-EMA), with three different EMA content and parent homopolymers were synthesized by emulsion polymerization. The chemical composition of copolymers were identified by FTIR, ^{1}H-NMR and ^{13}C-NMR spectroscopy. The thermal properties of copolymers were modified by changing the EMA content in copolymer compositions. Various amounts of LiClO$_4$ salt loaded (PAN-*co*-PEMA) copolymer films were prepared by solution casting. The dielectric properties of these films at different temperatures and frequencies were investigated. It was found that the dielectric constant and ac-conductivity of copolymer films were strongly influenced by the salt amounts and EMA content in copolymers. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 840–846, 2012

Key words: acrylonitrile; ethyl methacrylate; emulsion polymerization; dielectric constant; ac-conductivity

INTRODUCTION

Polyacrylonitrile (PAN) and its various copolymers have very wide applicational areas such as fiber technology, automotive industry, and membrane technology.[1–4] The kinetics of copolymerization of acrylonitrile (AN) with ethyl methacrylate (EMA) was investigated and the effect of the nature of solvents, temperature, initiator, and the monomer concentration on the rate of copolymerization were reported.[5,6] Brar and Saini studied the atom transfer radical copolymerization of AN and EMA at ambient temperature.[7,8] They reported the first-order kinetics when using 2-bromopropionitrile as an initiator. They also showed comprehensive microstructure of copolymer by 2D NMR techniques. Gupta and Sahoo[9] carried out the graft copolymerization of acrylonitrile and ethyl methacrylate on cellulose in the presence of cerric ions, which generate the active sites on the cellulose. They found the reactivity ratios for AN and EMA as 0.68 and 1.15, respectively. The different parameters such as cerric ion concentration, molarity, and composition of comonomer feed on grafting efficiency were investigated.

Hutchinson et al. examined the melt behavior and the mechanical properties of copolymer PAN with methyl acrylate (MA) and vinyl acetate (VA).[10] The crystal morphology and the melting temperatures of homopolymers were adjusted by the comonomers to reduce the copolymer melting temperature. The lengths of AN sequence were controlled to impart the paracrystalline order for mechanical stability, while keeping the melting point below the degradation range.

Recently, PAN-methacrylate based gel polymer electrolytes have drawn the attention for Li-ion batteries. Pu et al. prepared porous P(AN-MMA) membrane for gel electrolyte by emulsion polymerization.[11] Similarly, Fang Yua et al. produced solid polymer electrolytes (SPEs) from polyacrylonitrile-polyethylene oxide (PAN-PEO) copolymer and the influence of salt concentration, temperature, and molecular weight of PEO were examined.[12] Rajendran et al. prepared PVC/PEMA-based blend polymer electrolyte films containing lithium perchlorate (LiClO$_4$) as a salt by solvent casting technique.[13,14]

In this study, PAN, PEMA homopolymers, and P(AN-EMA) copolymers from 92/8 to 84/16*M* ratios were synthesized by emulsion polymerization

TABLE I
Recipes for PAN, PEMA, and P(AN-co-EMA) Synthesis

Acronym	AN (g)	EMA (g)	Surfactant (g)	APS (g)	1-dodecanthiol (g)	Water (mL)
PAN	22.45	–	1.80	0.0225	0.4266	43
PAN(92)-co-PEMA(8)[a]	22.02	4.12	2.09	0.0261	0.4967	55
PEMA	–	19.55	1.56	0.0196	0.3715	37

[a] A typical copolymer including 92 mol % of AN and 8 mol % EMA.

technique. This technique enables to obtain high molecular weight polymers with high polymerization rates in an environmentally friendly medium. The structural and thermal analyses were performed for all homopolymers and copolymers with different methods. Besides, the different amount of lithium perchlorate (LiClO$_4$) salt was added to copolymers to produce films and the electrical properties of these films were examined.

EXPERIMENTAL

Materials

AN (99%, Acros Organics) and EMA (99%, Acros Organics) were distilled under reduced pressure prior to use. Ammonium persulfate initiator (APS, 99+%, Acros Organics), 1-dodecanthiol chain transfer agent (98%, Merck) and DOWFAX 8390 surfactant were used as received. Magnesium sulfate (97% anhydrous, Acros Organics) and 1-methyl-2-pyrrolidonone (NMP; 99% Acros Organics) were used as received.

Synthesis of P(AN-co-EMA) and PEMA

The AN-EMA copolymers and their homopolymers were prepared by emulsion polymerization at 65°C. The detailed procedure has been described elsewhere.[15] In brief, the deionized water, surfactant, initiator, and chain transfer agent were added to the reaction flask followed by the premix of the monomer mixture (20% of total monomer). The remaining monomer mixture and the initiator were added dropwise. The resulting copolymers were precipitated with 1% aqueous MgSO$_4$ solution and the filtrate was washed with distilled water for several times. The copolymers were further purified in water with a Soxhlet apparatus and then dried in a vacuum oven at 60°C for overnight. The general recipe for polymerization is given in Table I.

Film preparation

A certain amount of lithium salt and copolymers were dissolved in DMF with various [Li$^+$]/[EMA] mole ratios of 0.2, 0.125, and 0.1. Films were pre-pared by solution casting on glass plate under IR lamp and then dried in vacuum at 60°C for 24 h.

Characterization

The ^{1}H-NMR spectra of the purified copolymers were recorded in d_6-DMSO using an Ultrashield 400 MHz Digital NMR Bruker spectrometer. The FTIR spectra of the samples were recorded on a Bruker Vertex-70 FTIR spectrometer with KBr pellets. Viscosities of the polymer solutions were measured with a capillary Ubbelohde viscometer in 1-methyl 2-pyrolidinone at 30°C. Differential scanning calorimetry DSC was performed with Perkin–Elmer Diamond DSC with a heating rate of 10°C/min. Nitrogen was used as the sweeping gas. TGA thermograms were taken on Perkin–Elmer Pyris 1 TGA under nitrogen atmosphere and polymer was heated from 35 to 1000°C with a heating rate of 10°C/min.

For dielectric measurements, the surfaces of the samples were covered with silver paste to form electrodes. The dielectric measurements were performed between 20 Hz and 1 MHz frequency range at different temperatures (300–400 K) by using Agilent 4284A LCR Meter. The real part of dielectric constant was calculated by using following equation:

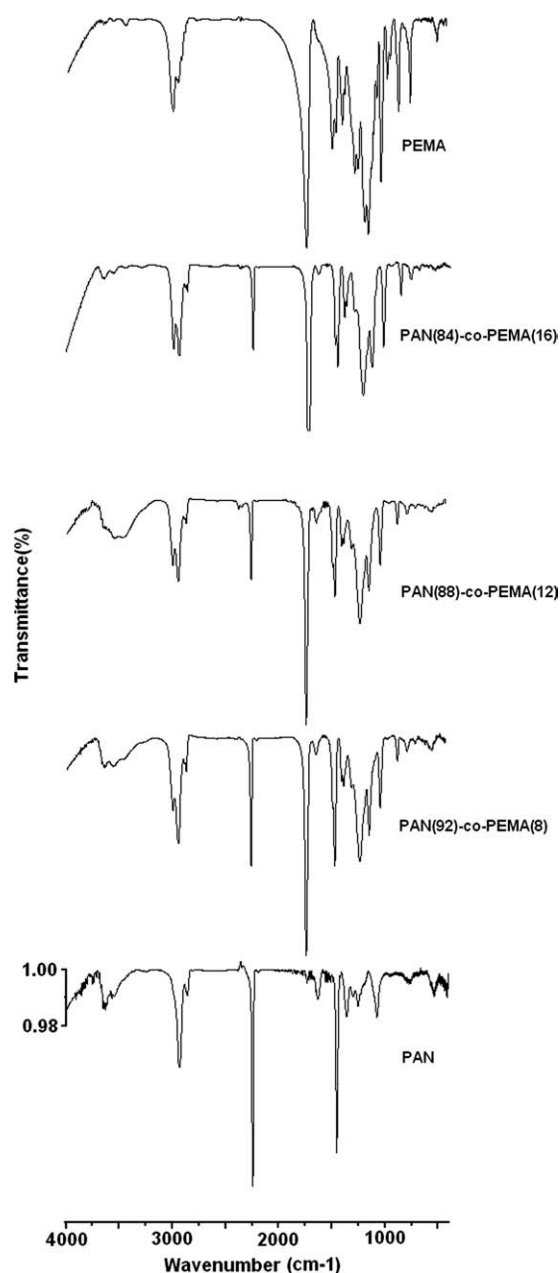$$\varepsilon' = \frac{C_p d}{\varepsilon_0 A}$$

where C_p is the capacitance of the sample, ε_0 (dielectric permittivity in vacuum) which is equal to 8.85×10^{-4} F/cm, A is the effective surface area, and d is the thickness of the samples. Ac-conductivities (σ_{ac}) of the samples were calculated with the following equation:

$$\sigma_{ac} = \frac{\omega C_p d \tan \delta}{A}$$

where $\tan \delta$ is the dielectric loss factor and ω is the angular frequency ($2\pi f$)

RESULTS AND DISCUSSION

The FTIR spectra of PAN, PEMA homopolymers and their copolymers are given in Figure 1. A broad

**Figure 1** FT-IR spectra of PAN, PEMA, and P(AN-*co*-EMA) copolymers.

and carbonyl (—C=O) stretching can be seen at 2243 and 1724 cm^{-1}, respectively. Both PAN and PEMA originated functional groups are identified in the FTIR spectra of copolymers.

The chemical structure confirmation and the co-polymer composition calculations were established by using ^{1}H-NMR spectroscopy. All protons were labeled in Figure 2 and copolymer compositions were calculated by the integral area (I) of the —OCH$_2$ (e) and methylene protons (a and c) using following equation.

$$\text{Mol percent of EMA} = \frac{I_e/2}{I_a/2 + I_c/2}$$

The —OCH$_2$ protons for the EMA units appeared at 4.1 ppm and the signals at 1.5–2.2 ppm were attributed to the backbone —CH$_2$ protons for both EMA and AN units. Table II shows the comonomer
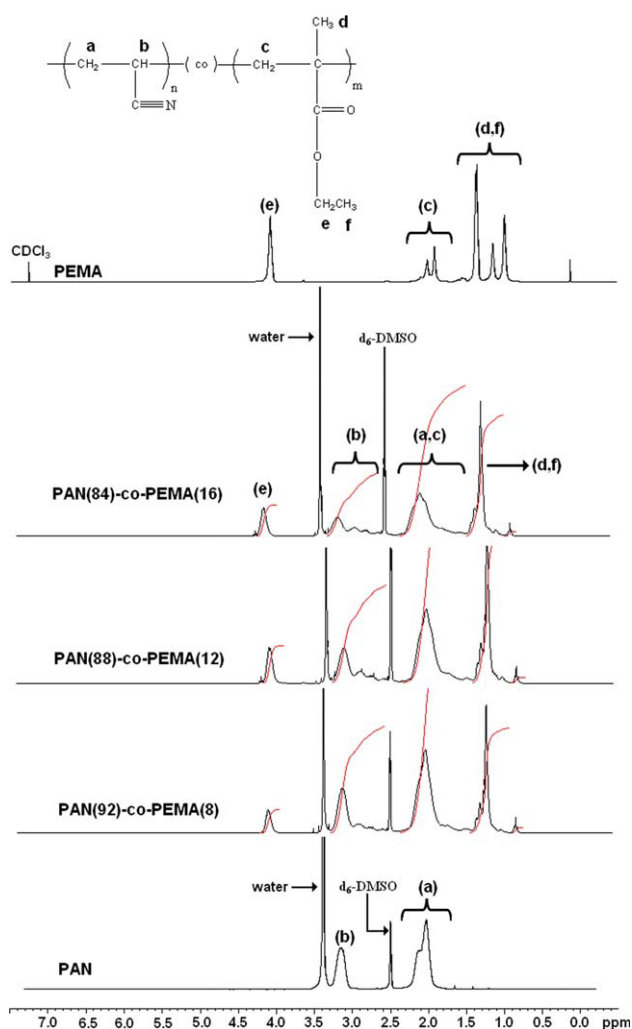
Figure 2 ^{1}H-NMR spectra of P(AN-*co*-EMA) copolymers from 92/8 to 84/16 mol %. [Color figure can be viewed in the online issue, which is available at wileyonline library.com.]

band at around 2989 cm^{-1} is attributed to the C—H stretching in methyl and methylene groups for PEMA. The strong C=O stretching is seen at 1734 cm^{-1} and C—H bending for —CH$_3$ and —CH$_2$ groups appeared at 1488 cm^{-1}. The broad absorption bands around 1272–1027 cm^{-1} is ascribed to the C—C(=O)—O and O—C—C ester groups. The methyl rocking vibrations can be seen at 968 cm^{-1}. In FTIR spectrum of PAN, the —C=N groups is observed at 2244 cm^{-1}. The C—H stretching and bending vibrations for —CH$_3$ and —CH$_2$ groups appeared at 2929 and 1456 cm^{-1}, respectively. For all copolymers, the characteristic nitrile (—C=N)

Comonomers in feed (mol %)[a]	Comonomers in polymer (mol %) AN/EMA[b]	$[\eta]_{NMP}^{30°C}$
PAN(92)-co-PEMA(8)	90.1/9.9	1.3
PAN(88)-co-PEMA(12)	84.3/15.7	0.8
PAN(84)-co-PEMA(16)	80.3/19.7	1.1

[a] By weight.
[b] By proton NMR.

mole fractions in the feed and in the copolymers. It can be seen that the comonomers were incorporated into the copolymer at almost the same feed ratios.

The chemical structures of PAN-PEMA copolymers were also clarified with ^{13}C-NMR (Fig. 3) and the assignment of the observed peaks of PAN and PEMA carbons are illustrated in the same figure. The characteristic —C≡N groups carbons corresponding to AN and the —C=O carbons relating to EMA were observed at 120 (b) and 174 (a) ppm, respectively. The other carbons concerned with the —CH$_3$(g), —CH$_2$(e), —CH(f), and —OCH$_2$(c) groups can be identified clearly at around 22, 33, 28, and 61 ppm, respectively. Kapur and Brar discussed the ^{13}C-NMR spectra of several AN/EMA copolymers in terms of their triad monomer sequence and cotacticity.[16]

The DSC thermograms of all copolymers exhibit one glass transition temperature (T_g) which is related with the copolymer compositions (Fig. 4). The T_g's of copolymers were reduced from 87 to 77°C with increasing EMA content in copolymers. The T_g's of random AN/EMA copolymers were also studied by Penzel et al.[17,18] and the T_g's of copolymers in good agreement with literature.

The thermal stabilities of the copolymers and homopolymers were elucidated by TGA method (Fig. 5). The decomposition temperatures, the 10% weight loss temperatures and the char yields of the samples were tabulated in Table III. The copolymers were degraded at higher temperatures than their parent homopolymers and also the 10% weight loss temperatures increases with increasing EMA content in the copolymers. Therefore, the thermal stabilities of copolymers were improved by the incorporation of the comonomers. Besides, the TGA analysis showed that the PEMA has less residual char than the PAN homopolymer and this trend was also observed for the copolymers.

High dielectric constant observed at low frequencies is an expected behavior for the polymeric materials have dipolar structures. At lower frequencies, dipoles have much more times to orient towards the external electric field and resulting in higher ε′ values. (Fig. 6) Because dipoles are not able to follow

the external field variation at higher frequencies, so the ε′ values decreases monotonically with increasing frequencies.[19,20]

As can be seen in structure of copolymers PEMA has high density dipolar side groups. This explains the increase in ε′ values depending on PEMA content.[21,22] Therefore the sample has highest PEMA
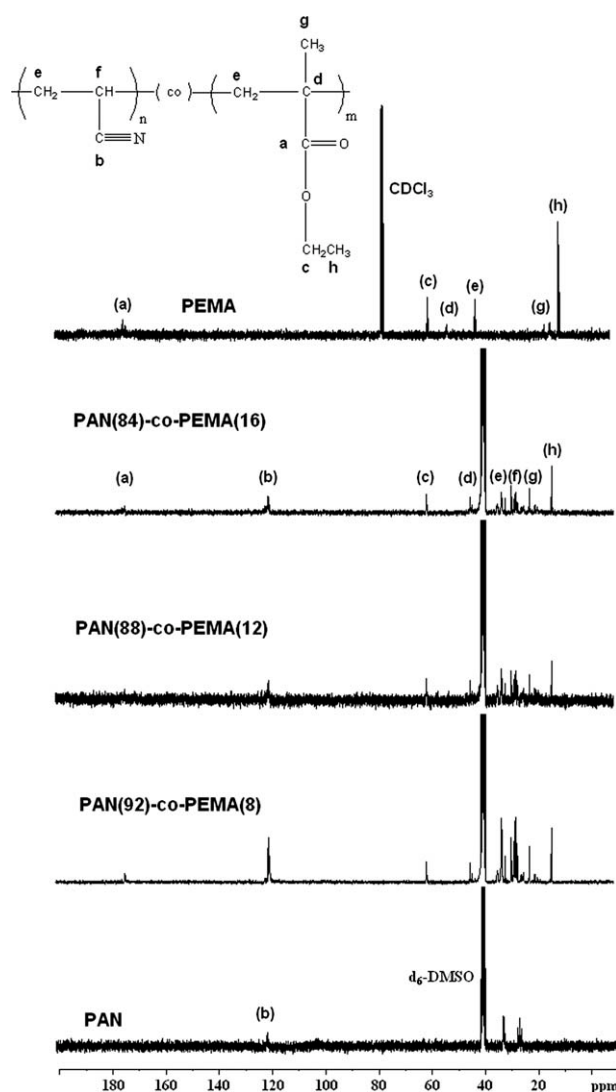
Figure 3 ^{13}C-NMR spectra of P(AN-co-EMA) copolymers from 92/8 to 84/16 mol %.

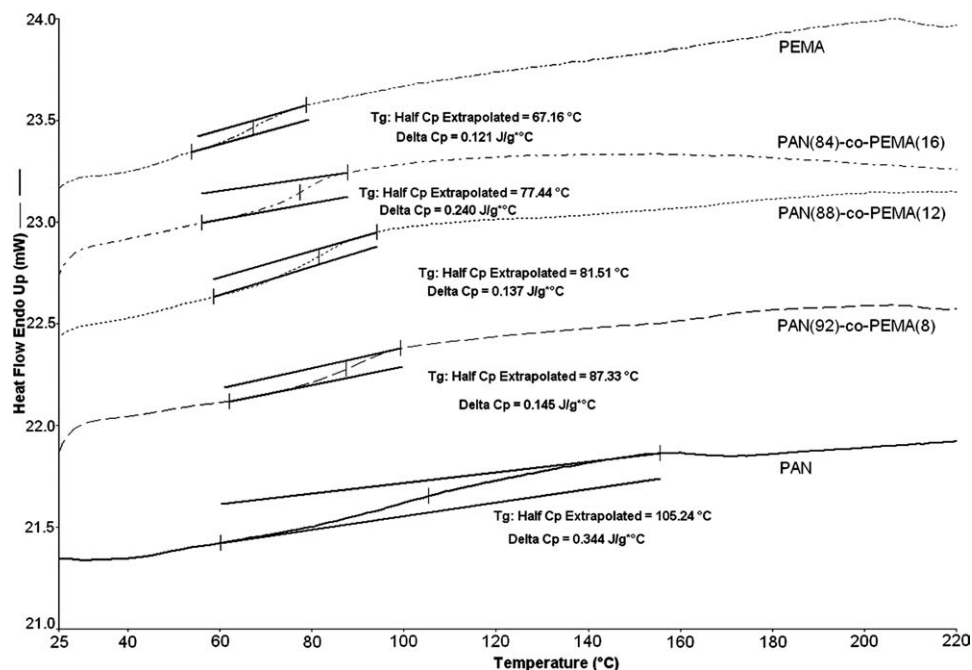**Figure 4**   DSC curves of P(AN-*co*-EMA) copolymers from 92/8 to 84/16*M* ratios and homopolymers.

content [PAN(84)-*co*-PEMA(16) + LiClO$_4$(0.2)] has highest ε′ value. At the same time, if the samples have same composition but diferent content of LiClO$_4$ are compared, it can be seen that the sample with higher salt content [PAN(84)-*co*-PEMA(16) + LiClO$_4$ (0.2) and PAN(88)-*co*-PEMA(12) + LiClO$_4$ (0.2)] has higher ε′ value. In this case, it can be said that doping process facilitate the orientation of the electrical dipoles.[20]

When the same low frequency range but different temperatures are compared [Fig. 6(a,b)], ε′ has higher value at 380 K. This situation can be explained as follow: As temperature is increased, free volume around the polymer chain increases and

facilitates easier move of dipole components, hence leading to a higher ε′ values.[19,22]

Figure 7 shows the temperature dependence of real part of dielectric constant. Around the glass transition region (350—400 K) there is a rapid increase in values of ε′. This can be interpreted as the easier movement of dipoles with increasing temperatures. Thermal mobility of the dipoles at higher temperatures increase significantly, therefore dipoles are able to move more easily within the structure, so it results in higher ε′ values.[19,22,23] It was found the correlations between the DSC results of copolymers and temperature effect on dielectric properties of copolymers. On the other hand, at certain temperature and frequencies, real part of the dielectric constant increases systematically with increasing PEMA content in the copolymer. This situation can be attributed to the increase in the amount of PEMA which has dipolar side groups orienting towards the external electric field.[22] Furthermore, above the glass
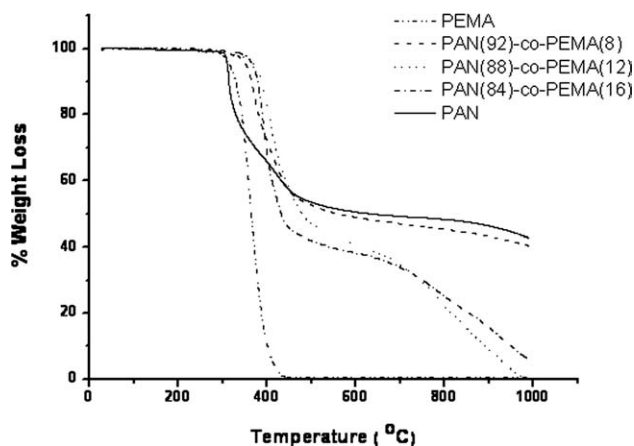

Figure 5   TGA thermograms of P(AN-*co*-EMA) copolymers and homopolymers; all samples are thermooxidatively stable.

TABLE III
TGA Data for Homopolymers and Copolymers

Samples	T_{10}[a] (°C)	T_d[b] (°C)	Char yield at 900°C
PEMA	330	364	0.8
PAN(84)-*co*-PEMA(16)	379	392	15.7
PAN(88)-*co*-PEMA(12)	388	399	8.6
PAN(92)-*co*-PHEA(8)	365	371	43.3
PAN	310	310	46.4

[a] 10% weight loss temperature.
[b] Decomposition temperature.
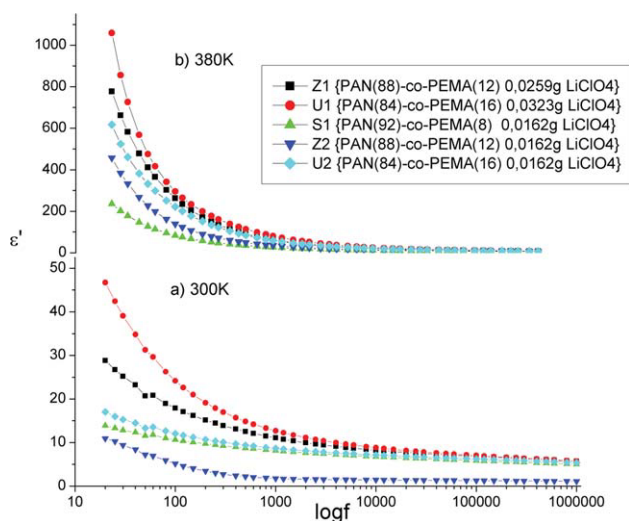
Figure 6 Frequency dependency of real part of dielectric constant (ε'); (a) 300 K and (b) 380 K. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

transition region, also increament in the amount of LiClO$_4$ effective in increasing ε' values. This situation, as mentioned above, can be explained with higher dipol momentum of the structure.

Figure 8 illustrates the temperature dependency of ac-conductivity. It can be seen that, the sample with highest PEMA content [PAN(84)-*co*-PEMA(16) + LiClO$_4$ (0.2)] has highest ac-conductivity and highest rate of increment with temperature. In this sample, highest PEMA and LiClO$_4$ content providing higher volume between chains and facilitates movement of ions of LiClO$_4$ and resulting in higher ac-conductivity.[19] At the same time, the samples with more salt content [PAN(84)-*co*-PEMA(16) + LiClO$_4$ (0.2) and PAN(88)-*co*-PEMA(12) + LiClO$_4$ (0.2)] show higher ac-conductivity. This can be explained due to the
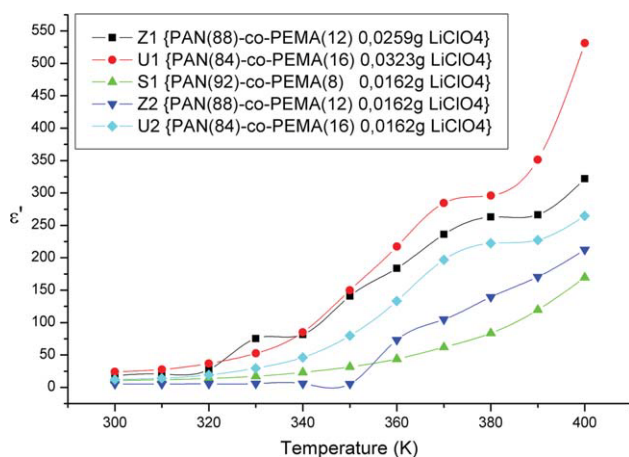
Figure 7 Temperature dependency of real part of dielectric constant (100 Hz). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
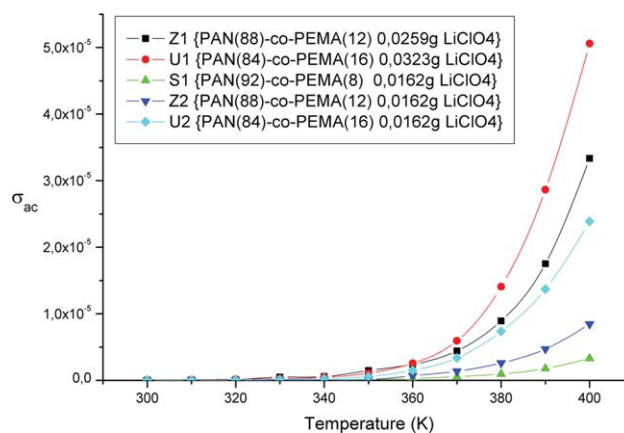
Figure 8 Temperature dependency of ac-conductivity (σ_{ac}) (100 Hz). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

rise in the number of charge carriers.[19,20,24] On the other hand, ac-conductivity of the all samples show an increase after 350 K. When temperature increases, due to the increasing vibration of polymer chain segments, neighboring atoms create a small amount of space surrounding its own volume in which vibrational motion can occur. Therefore increasing free volume around the polymer chains causes the mobility of the ions to increase. Hence, increasing the temperature causes the conductivity to increase due to the increased free volume and ionic and segmental mobilities.[19,20,25]

CONCLUSION

FTIR, ^{1}H-NMR, and ^{13}C-NMR results showed that the P(AN-*co*-EMA) copolymers were synthesized successfully and monomer feed ratios were comparable with copolymer composition. The thermal properties (i.e., T_g and decomposition temperatures) of copolymers were tailored by changing EMA content in copolymers. The dielectric measurements also indicated the influence of EMA comonomer and LiClO$_4$ salt amounts on the electrical properties of copolymer films. The copolymers with higher EMA and salt content showed the higher dielectric constant and the highest ac-conductivity.

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