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New sulfonated copolymers of acrylonitrile obtained by plasma-induced polymerization

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Summary

Ultrahigh molecular weight copolymers of acrylonitrile (AN) with sodium salt of trans-3-(4-sulfo-phenylcarbamoil)-acrylic acid (S) were obtained by plasma-induced polymerization (PIP) in water solutions. The copolymerization parameters were established and some structural and physical characterizations by thermally stimulated depolarization currents (TSDC) spectroscopic analysis of the S-AN copolymer were performed.

Introduction

In some previously published papers, PIP was reported, the results suggesting a possible direct synthesis of ultrahigh molecular weight polymers [1-8]. The copolymers of AN with S synthesized by PIP could be of interest for (a) synthetic fibers industry, in order to improve some properties (e.g. affinity for dyes, hydrophilicity) of polyacrylonitrile (PAN), and (b) oil producing industry, in order to replace the hydraulic cement, normally used in cementing jobs, into a different material consisting of long polymers with a low density and/or high durability [9, 10]. For both potential uses these S-AN copolymers must have ultra-long chains and must contain a high percent of acrylonitrile, the presence of –CN groups determining good intra-molecular cohesion, high thermal stability and mechanical resistance.

Acrylic homopolymers and copolymers, especially PAN, are compounds whose structure and structural changes have remained a difficult problem to elucidate. From this reason, the origin of the thermal transitions in PAN has not been uniquely determined. The published data indicate that the glass transition temperature, Tg, of PAN is scattered over a range of temperature (7°…140°C) [11-13] depending on the experimental method used and on the procedures of preparing the sample. This parameter is generally correlated with copolymer composition, microstructure and sequence distribution of monomeric units in copolymer. As TSDC spectroscopic analysis commonly works in the range of equivalent frequencies of 10^{-2}-10^{-4}Hz, and could be an useful complementary tool for the molecular motion, structure and transition studies of the macromolecular compounds, this method was used to investigate some properties of the new S-AN copolymers.

Experimental

The experimental apparatus and general technique of PIP are described in previously published papers [3, 4], but in this paper a simple scheme of the experimental set-up is shown in Figure 1.

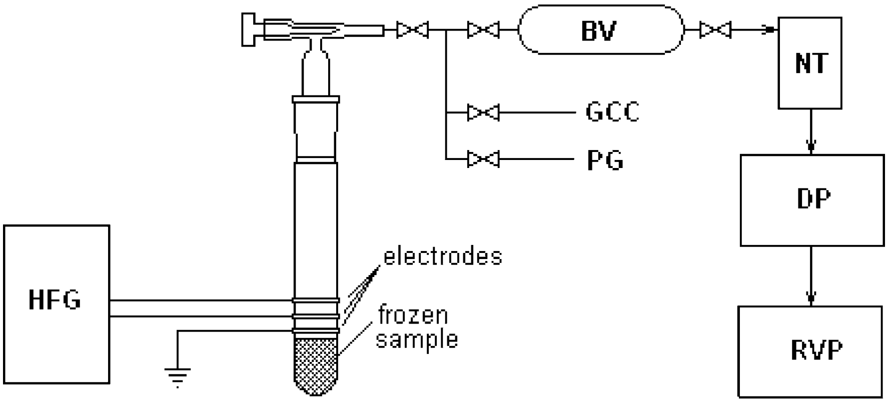

Figure 1. Experimental set-up for plasma-induced polymerization; HFG – high frequency generator; BV – buffer vessel; NT – nitrogen trap; DP – diffusion pump; RVG – rotary vacuum pump; PG – Pirani gauge; GCC – cold cathode gauge

S monomer [14] of 99.9% was used without further purification and AN monomer, reagent grade from Fluka, was distilled under reduced pressure immediately prior to use. Pre-weighted amounts of co-monomer mixture solutions in deionized water were introduced in polymerization Pyrex ampoules, degassed by repeated freezing and thawing under vacuum and finally frozen in liquid nitrogen and sealed at 10^{-2}-10^{-3} torr. Electrical discharge was then operated between two external electrodes, located on each ampoule at 3 and 4 cm, respectively, from the frozen sample and coupled to a high frequency generator (2.5MHz, 100W). The discharge was operated during 60 sec. The initiation period was followed by post-polymerization period (t_{pp}), during that the ampoules were kept in dark, in a constant temperature bath (24°C). In order to keep low and never exceed 10% the conversion values, the post-polymerization time was established between 4 and 6 hours (t_{pp} increasing with the increase of S co-monomer content in the initial mixture). In all cases, the obtained copolymers were insoluble in the reaction medium and were purified by re-solvation in dimethylformamide (DMF) (Fluka) and re-precipitation in deionized water. The purified copolymers (white powder) were dried at 50°C under vacuum for 48 hours, for the complete removal of the solvent (DMF) which tends to be bound to the polar groups of the polymer. As the studied copolymerization system is a new one, a control experiment was performed in identical conditions but using classical radical initiators (ammonium peroxydisulfate/sodium metabisulfite, 58°C).

Intrinsic viscosities [η] were determined in DMF solutions at 30(±0.2) °C on a standard Ubbelhode viscometer. The polymer solutions for [η] measurements were prepared with special cautions taking into account that (a) harsh agitation can physically break long macromolecules and (b) the rate at which very large polymers go into solution can be so low since it requires long time of gentle mixing to obtain true solution equilibrium conditions. If these don't exist, then the polymer aggregates remaining will falsify all characterization results. In order to respect the dilution condition for high molecular weight polymers characterization [15], in our determinations were used polymer solutions at polymer concentrations of maximum 100ppm, for keeping the overlap parameter from Einstein relation [16] less than one.

Structural confirmation for copolymerization products was obtained by IR spectroscopy (Specord M80 Zeiss instrument, KBr pellets). The copolymer compositions were determined by ^{1}H NMR spectroscopy, from the ratio of signal integrals at 2.1ppm (aliphatic protons of -CH_2- from AN) and 7.8 ppm (aromatic protons from S). The spectra were registered on a Varian Gemini 300 BB instrument operating at 300 MHz, in DMSO-d_6 solutions, at 60°C.

Samples used for TSDC measurements were disk-shaped, prepared by compressing the compound powder in a mold under a pressure of 10^5 N/cm^2, and films, prepared by controlled evaporation of DMF copolymer solution of 0.4 wt% under vacuum at 1 torr. Both 16 mm – diameter disks and films were provided with vacuum evaporated silver electrodes of circular form. In order to prevent current leakage on surface, the electrodes had a diameter of only 14 mm and were centrally placed on both sides of the disks and films, respectively. TSDC measurements were carried out in dry nitrogen using a device presented in a previously published paper [17]. The thermal cycles of polarization and depolarization of samples consisted on the following steps. A sample with polarization field E_p was warmed up to the polarization temperature T_p, which was maintained constant for a polarization time t_p. After cooling to -20°C using liquid nitrogen, E_p was removed and the sample was short-circuited for 10 min in order to eliminate the rapid depolarization currents; then, the depolarization currents were recorded at a heating rate of 3.3°C/min.

Results and discussion

1. Polymerization data

The IR spectra (Figure 2) evidently confirm the formation of the S-AN copolymers [18].

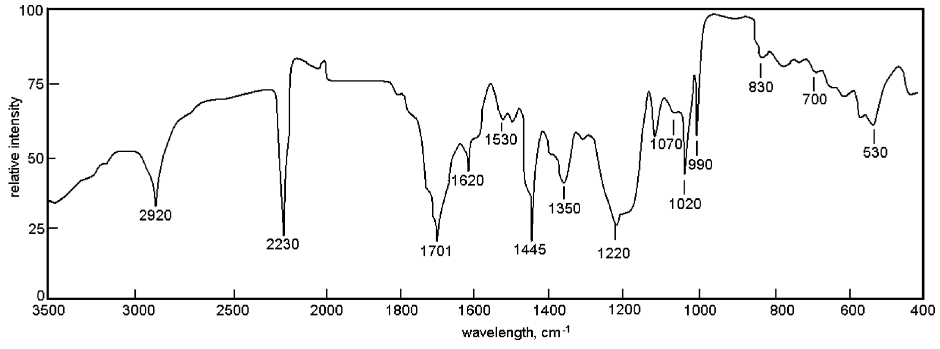

Figure 2. IR spectrum of S-AN copolymer, sample 2

Copolymerization and structural data obtained from ^{1}H NMR spectra are summarized in table 1 and the copolymerization diagram is presented in Figure 3. Monomer feed ratios and experimentally determined values of copolymer composition were used to evaluate monomer reactivity ratios for the S-AN copolymers.

Table 1. Copolymerization* and structural** data for $S(M_1)/AN(M_2)$ copolymers obtained by PIP

Sample P(S-AN)	Feed*** composition $[M_1]/[M_2]$	Conv. %	Copolym. composition $d[M_1]/d[M_2]$	Contact type (probability)			[η] dL/g
				f_{222}	f_{122}	f_{121}	
1	0.061	9.8	0.013	0.97835	0.02154	0.00013	9.3
2	0.176	7.6	0.036	0.93080	0.06795	0.00120	9.6
3	0.333	8.5	0.091	0.87490	0.12085	0.00526	11.0
4	0.538	9.2	0.148	0.80910	0.18071	0.01051	12.8
5	1.000	9.7	0.275	0.68501	0.28399	0.03101	14.9
6	3.000	9.5	0.666	0.43502	0.46790	0.09695	18.1
7	4.000	8.7	1.017	0.15010	0.65960	0.18999	18.9

* from ^1H NMR spectra
** statistically calculated from reactivity ratios
*** for 5% wt monomers in water

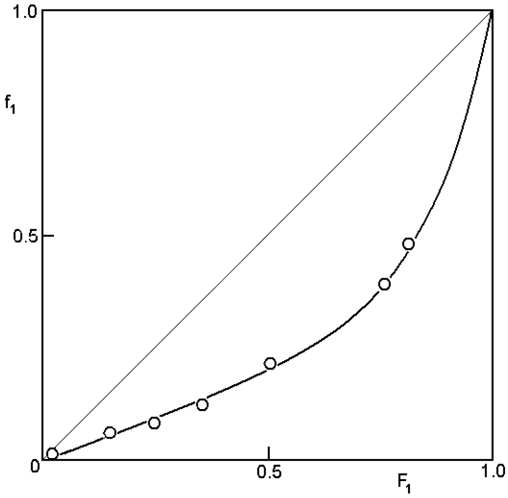

Figure 3. Copolymerization diagram for $S(M_1)/AN(M_2)$ system (F_1=mole fraction of S in the feed; f_1=mole fraction of S in the copolymer)

The Kélen-Tüdös method [19] was used to determine reactivity ratios at low conversion. In Figure 4 the Kélen-Tüdös plot for the copolymerization of $S(M_1)$ and $AN(M_2)$ is represented. The obtained reactivity ratio values are $r_1 = 0.35 \pm 0.06$ and $r_2 = 4.82 \pm 0.003$. We did not take into account the effect of the number of meaningful experimental data on the fitness of the theoretical copolymerization models [20].

In the control experiment were calculated, also by Kélen-Tüdös method, the reactivity ratios for classical radical copolymerization of $S(M_1)$ and $AN(M_2)$, and the obtained values are of the same order of magnitude as those obtained for PIP: $r_1 = 0.1 \pm 0.04$ and $r_2 = 4.18 \pm 0.002$. For both cases, the obtained values for reactivity ratios are in agreement with steric and electrostatic factors. The straight line in Kélen-Tüdös plot indicate that no penultimate effect seems to exist for plasma-induced copolymerization of AN with S and that the terminal model of copolymerization could be considered to describe the process.

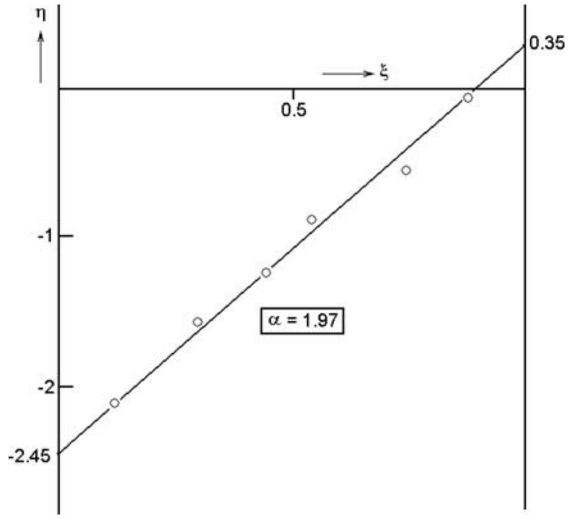

Figure 4. The Kélen-Tüdös plot for S(M_1)/AN(M_2) system

Considering this statistical model (Markov of first order), it was calculated triad sequence fractions with AN(M_2) central unity according to Harwood and Ritchey [21]; the obtained data are presented in table 1.

Intrinsic viscosities data (table 1) show that introducing S units into the macromolecular chain of PAN an increase in [η] occurs as a consequence of the expansion of the polymer coil in solution due to the repulsive forces (both intramolecular coulombic repulsion from the ionic groups and steric repulsion). Especially, the [η] values suggest ultralong macromolecular chains (e.g., in the case of PAN obtained by PIP, for [η] =6.44dL/g, determined in DMF solutions at 30°C, the value of the weight average molecular weight is 1.132×10^6 [22]).

2. Thermic transitions data

The TSDC thermograms of PAN, P(S-AN)$_1$ and P(S-AN)$_2$ synthesized by PIP in the temperature range of 50…250°C are comparatively presented in Figure 5.

All spectra have the same general shape and are characterized by one current peak (α) more or less resolved, and an increasing current part (ρ) at higher temperatures. The α peak of P(S-AN)$_2$ is well resolved, whereas in the case of P(S-AN)$_1$ and especially for PAN, this peak is overlapped by ρ increasing current, which is probably the increasing portion of a new arising peak. In order to keep the structure of polymers unchanged, the samples were not warmed up over the temperatures shown in Figure 5.

TSDC spectra show that both intensity and temperature of the α peak are appreciably affected by the copolymer composition. The maximum intensity decreases with the S content, whereas the corresponding temperature values increase. The α peak temperature of PAN, shown in Figure 5, appears to be close to the glass transition temperature (140°C) reported elsewhere [23, 24]. The S comonomer is bulky and more polar as compared to the AN monomer. The introduction of S unities into the polymer chain enhances the dipole-dipole interactions between adjacent chains and shortens the AN segments of chains.

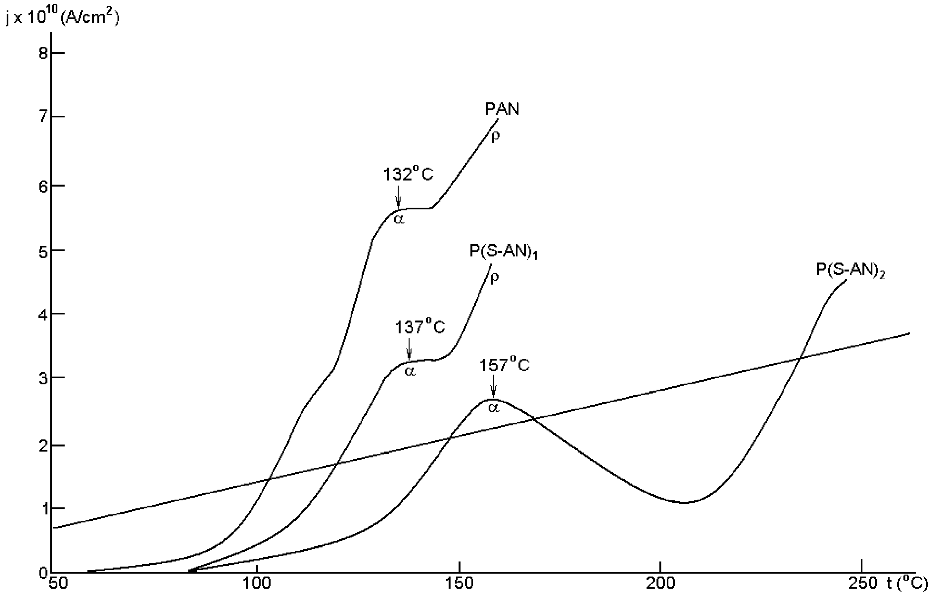

Figure 5. TSDC spectra of PAN, P(S-AN)$_1$ and P(S-AN)$_2$; polarizing conditions: E_p= 10 kv/cm; t_p = 30min; T_p = 150°C for PAN, P(S-AN)$_1$ and 200°C for P(S-AN)$_2$

This two facts result in an increasing of the T_g temperature of the copolymers. If the α peak observed for PAN is associated to the glass transition, then it is reasonable to suggest that the α dielectric peaks observed for P(S-AN)$_1$ and P(S-AN)$_2$ are related to the second-order transition (Tg) of these copolymers.

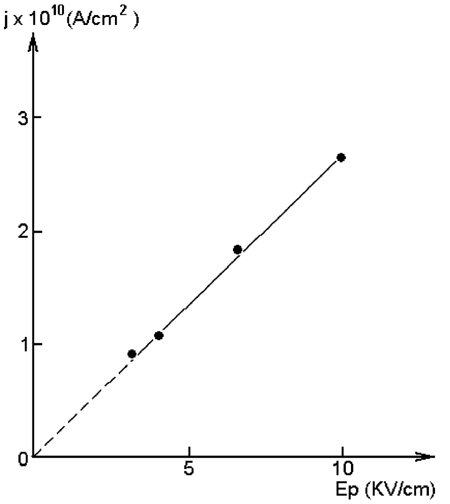

Figure 6. Plot of maximum current of the α peak of P(S-AN)$_2$ vs. polarizing electric field; the other polarizing conditions are as indicated in the legend to Figure 5

The value of this parameter is correlated with the composition of the copolymer and increase if the amount of S in the copolymer increases. It is not clear from these initial results whether or not this type of variation should be expressed directly as a function of the copolymer composition, or whether it should be considered in terms of diad or even triad distributions [25]. The polarizing field dependence of the maximum current of the α peak for $P(S\text{-}AN)_2$ is shown in Figure 6. The existence of a strict proportionality between the maximum intensity and field strength shows that a uniform volume polarization is taking place [10]. Given that the straight line passes through the origin, the volume polarization is of dipolar nature. This finding also supports the fact that the observed α peaks are related with the second order transition. Since the maximum intensity of the α peak decreases with increasing S comonomer content, the micro-brownian motions involved in the polarization process occur in the AN segments of the copolymer. The polymer film presents a similar TSDC spectrum to that of polymer disk (Figure 7); the α peak is well resolved and is located at the same temperature in both cases.

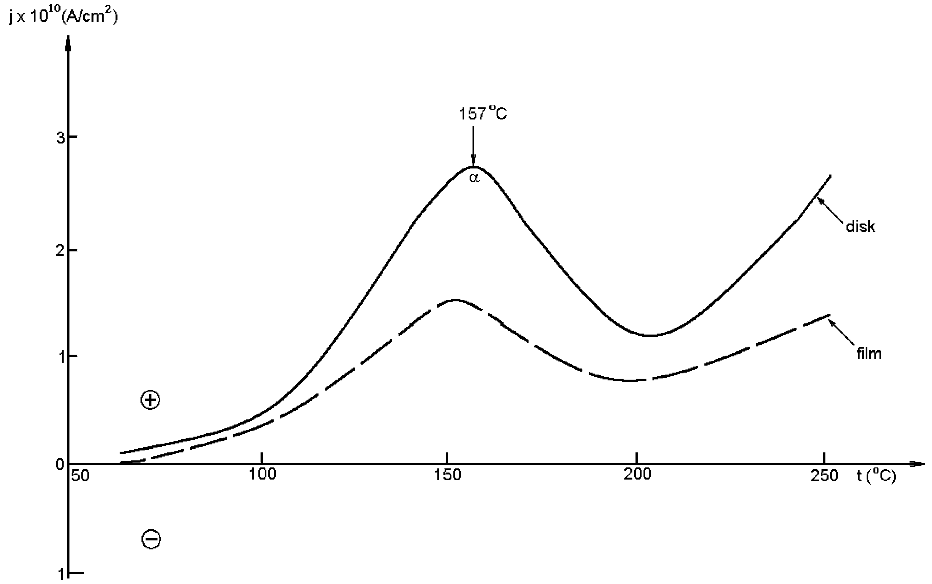

Figure 7. TSDC spectra of disk and film $P(S\text{-}AN)_2$ samples; conditions from legend to Fig. 5

Conclusions

The plasma-induced copolymerization of sodium salt of trans-3-(4-sulfo-phenyl-carbamoil)-acrylic acid with acrylonitrile was studied and the copolymerization parameters were established. Using the experimentally determined reactivity ratios and classical statistical relationships, it is possible now to synthesize by this method model copolymers S-AN, with controlled structure.

Both the viscosimetric and TSDC spectroscopic data motivate the interest for these copolymers. The determined intrinsic viscosity values suggest very high molecular weights for the products. The TSDC spectra depend on the copolymer composition. The α peak observed was related with T_g of the copolymers.

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