Terpolymerization of styrene, acrylonitrile and chromium acrylate: synthesis and properties

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Solution terpolymerization of styrene, acrylonitrile and chromium acrylate has been carried out in dimethylformamide at 85°C using styrene–arsenic sulfide complex as radical initiator. ^{1}H nuclear magnetic resonance (n.m.r.), infra-red (i.r.) and elemental analysis have been used to characterize the terpolymer. Data from ^{1}H n.m.r., elemental analysis and gravimetric analysis have been used to evaluate terpolymer composition. Reactivity ratios (calculated from Finemann–Ross method as $r_1(\mathrm{Sty}) = 5 \pm 2$ $r_2(\mathrm{AN+CrA}) = 0.15 + 0.02$) and composition confirm its random origin. The terpolymer was highly thermally stable and has a glass transition temperature of 96°C as evaluated from differential scanning calorimetry studies.

(Keywords: terpolymerization; styrene–acrylonitrile; chromium acrylate)

INTRODUCTION

Polymerization reactions involving more than two monomers have been under investigation since the systematic study of polymer science began in the 1930s. During that early period it was recognized that these reactions possessed unique features, which distinguished them from homopolymerization and also made their interpretation more difficult. Terpolymerizations have continued to evoke interest to both academic and industrialist alike, and one of the main advantages of this technique is that it provides a convenient method of synthesizing new polymeric structures with wide range of properties, i.e. to modify polymer properties.

The problem of terpolymerization is readily approached through application of the concepts and techniques already developed for two-component systems. Multicomponent polymerization, especially terpolymerization, allows the development of information on a certain class of monomer not otherwise available. Although voluminous literature is available for homo- and copolymerization, very little kinetic and synthetic information is available for terpolymerization. This is because of wide variation in monomer reactivity with radicals.

However, a search of the literature reveals that a few ternary polymerization systems have been reported: methyl methacrylate–styrene–butadiene terpolymer[1]; acrylonitrile, styrene and esters of cyanocinnamic acid[2]; styrene–methyl methacrylate–methyl acrylate[3]; acrylonitrile–methyl methacrylate–methacrylic acid[4]; maleic acid terpolymer[5]; tributyltin acrylate–methyl acrylate–styrene allyl methacrylate, and butyl methacrylate, butyl acrylate and acrylonitrile[6]; butadiene–acrylonitrile–chlorocyclohexyl vinyl ketone[7]; acrylonitrile–methacrylate–itaconic acid[8]; 7,7,8,8-tetrakis(ethoxycarbonyl)quinodimethane (TECQ), maleic anhydride and 2-chloroethyl vinyl ether or *p*-chlorostyrene[9]; acrylonitrile–styrene–maleic anhydride[10]; maleic anhydride–ethyl hexyl acrylate–styrene[11]; acrylonitrile, styrene and 2,4,6-tribromophenyl acrylate[12]; *N*-acryloyloxyphthalimide or *N*-methacryloyloxy phthalimide with methyl acrylate–methylmethacrylate and acrylonitrile[13]; and styrene–vinylpyrrolidone–acrylonitrile[14].

The present article details the synthesis of a terpolymer involving e$^-$ donor (styrene, Sty), e$^-$ acceptor (acrylonitrile, AN) and metal-containing monomer (chromium acrylate, CrA) as starting material, its characterization and some of its end properties.

EXPERIMENTAL

Materials

The monomers styrene, acrylonitrile and chromium acrylate were purified by standard methods. As_2S_3 was used as received.

Synthesis of styrene–arsenic sulfide complex

The complex was synthesized by a method reported elsewhere by us[15–17].

Preparation of chromium acrylate

This has been prepared by the procedure given in the literature[18].

Synthesis of terpolymer

Terpolymers of styrene and AN with chromium acrylate were obtained by solution polymerization in

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Table 1 Elemental analysis data

Sample No.	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Chromium (%)	Oxygen (%)
R_1	67.18	6.13	7.18	3.9	15.61
R_2	72.13	5.55	5.03	4.3	12.99
R_3	62.0	6.06	9.44	1.74	20.31
R_4	76.7	5.23	10.14	6.0	1.93
R_5	69.37	6.4	5.58	4.9	13.75
R_6	74.11	6.29	8.94	6.9	3.76

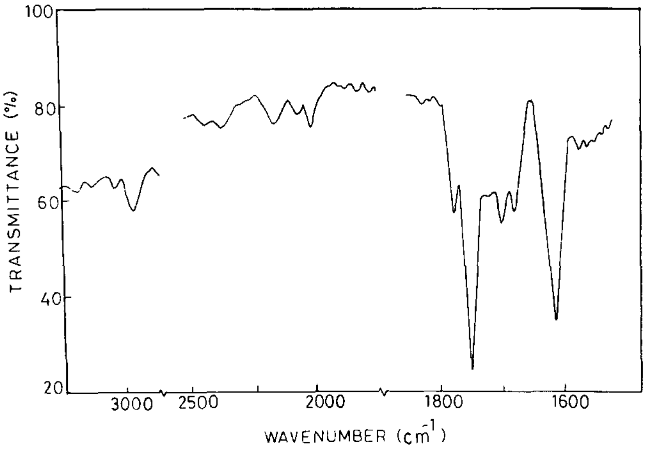

Figure 1 I.r. spectrum of terpolymer

dimethylformamide (DMF) at 85°C for one hour under an inert atmosphere of nitrogen in the presence of styrene–arsenic sulfide complex as radical initiator. The terpolymer precipitated with water was dried to constant weight. It was then refluxed with cyclohexane, acetonitrile and toluene to remove homo- and copolymers. A total weight loss of approximately 3–4% was observed.

CHARACTERIZATION

Viscosity

The viscosity of the synthesized terpolymer was obtained using an Ubbelohde viscometer at room temperature (35°C) in dioxane.

Infra-red spectrum

The infra-red spectrum was recorded on a Perkin–Elmer spectrometer (599 B).

N.m.r. spectrum

^1H n.m.r. spectra were recorded on a Varian 100 HA spectrophotometer.

Specific conductivity

This was measured by a Digital Keithley electrometer (model 614).

Elemental analysis

Elemental analysis (C, H, N) was performed on a Perkin–Elmer 240 C elemental analyser. Chromium was estimated by gravimetric analysis.

Thermal analysis

Thermogravimetric analysis (t.g.a.) was carried out on a Stanton Redcroft at a heating rate of 15°C min^{-1} under nitrogen atmosphere.

Differential scanning calorimetry

D.s.c. was carried out on a DuPont 910 C differential scanning calorimeter at a heating rate of 20°C min^{-1} under nitrogen atmosphere.

RESULTS AND DISCUSSION

The polymerization conditions and results are summarized in *Tables 1* and *2* and *Figures 1–5.*

Characterization of terpolymer

The terpolymer is soluble in benzene, acetone, dimethylformamide, ethyl acetate and dioxane and is insoluble in alcohol, e.g. isopropanol and methanol.

Elemental analysis

Nitrogen percentage in terpolymer has been calculated from elemental analysis. The values were 7.18, 5.03, 9.44, 10.14, 5.58 and 8.94 from R_1 and R_6, respectively. The chromium content has been calculated from gravimetric analysis and the results are summarized in *Table 1.*

Infra-red

From *Figure 1*, assignments are (KBr): 3000 cm^{-1}, aromatic C–H stretching; 600–700 cm^{-1}, C–H bending; 1600–1750 cm^{-1}, C=O acrylate; and 2240 cm^{-1}, C≡N.

Nuclear magnetic resonance

From *Table 2* and *Figures 2* and *3*, δ (ppm) (TMS): 7.0–8.1 (m, phenyl protons), 1.5–2.18 (m, CH, CH_2) for sample R_5; and 7.4–8.1 (m, phenyl protons), 1.5–2.0 (m, CH, CH_2) for sample R_6.

Reactivity ratios

The above band peak positions and results from elemental analysis confirm the presence of styrene, acrylonitrile and chromium acrylate units in the terpolymer chain. In order to calculate the reactivity ratios, the composition of styrene content from the peak area of phenyl protons, acrylonitrile content from N% and chromium content from gravimetric analysis have been calculated. Composition of terpolymer has been shown in *Table 2.* A study of *Table 2* reveals that the sum of mole fractions of e^- acceptor monomer (CrA + AN) and e^- donor monomer (Sty) is not equimolar; hence the terpolymer is of random origin. This observation was

Table 2 Terpolymer composition[a]

Sample No.	Monomer feed ratio [Sty/(AN+CrA)]	Terpolymer composition (mole fraction)		
		Sty[b]	AN[c]	CrA[d]
R_1	0.76	0.84	0.14	0.014
R_2	0.33	0.81	0.152	0.034
R_3	0.52	0.64	0.34	0.016
R_4	0.521	0.78	0.186	0.029
R_5	0.53	0.78	0.173	0.040
R_6	0.87	0.79	0.17	0.030

[a] $[As_2S_3] = 6.7 \times 10^{-3}$ mol l^{-1}, polymerization time = 60 min, polymerization temperature = 85 ± 0.1°C

[b] Calculated from n.m.r. peak due to phenyl protons

[c] Calculated from elemental analysis data (N%)

[d] Calculated from chemical analysis

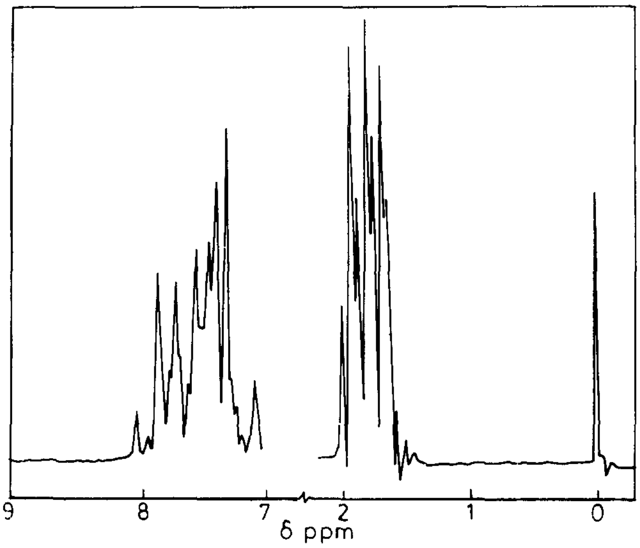

Figure 2 N.m.r. spectrum of terpolymer (R_5)

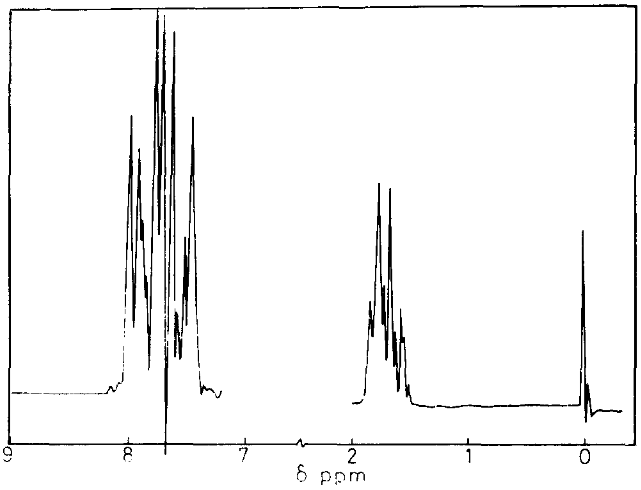

Figure 3 N.m.r. spectrum of terpolymer (R_6)

further strengthened by the following facts:

(i) formation of homopolymers and copolymers, as suggested by weight loss in solvent treatment of terpolymer; and

(ii) calculation of reactivity ratios by Finemann–Ross method[19] as $r_1(\mathrm{Sty}) = 5 \pm 2$ and $r_2(\mathrm{AN} + \mathrm{CrA}) = 0.15 \pm 0.02$.

The results show that there are wide variations in reactivity ratios of e^- donor and e^- acceptor monomers justifying the higher styrene content in the terpolymer chain and suggesting that the incorporation of acrylonitrile and chromium acrylate in appreciable quantity will be very difficult.

Properties

The terpolymer is crystalline and has its softening temperature ranges from 200 to 225°C.

The terpolymer was highly thermally stable up to 400°C and has a glass transition temperature of 96°C as evaluated from d.s.c. *Figure 4* shows the transition melting range originating from 380°C. This is followed by decomposition of the terpolymer[20].

The t.g.a. curve (*Figure 5*) shows the weight loss *versus* temperature of the terpolymer of styrene, acrylonitrile and chromium acrylate. The total weight loss at a given stage is as follows: 25–75°C, 4%; 100–200°C, 8%; 200–350°C, 8%; 350–450°C, 64%. The results show that maximum polymer degradation occurs between 350 and 450°C.

The moisture uptake of terpolymer was 5.28% at 110°C for 24 h.

The terpolymer passed the corrosion test (48 h).

The terpolymer shows signs of electrical conductivity as evidenced from the following result at 35°C: specific conductivity of terpolymer (0.34%) in ethyl acetate $= 0.8\,\Omega$; specific conductivity of ethyl acetate $= 0.4\,\Omega$.

The intrinsic viscosity of the terpolymer ranges from 0.30 to 0.50 dl g^{-1}.

CONCLUSION

It may be concluded that styrene–arsenic sulfide complex can be used to carry out synthesis of Sty–AN–CrA random terpolymer with improved thermal properties.

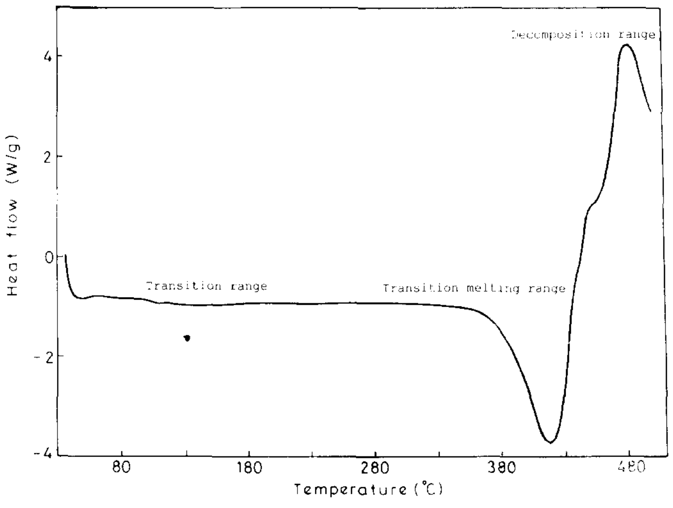

Figure 4 D.s.c. curve of terpolymer

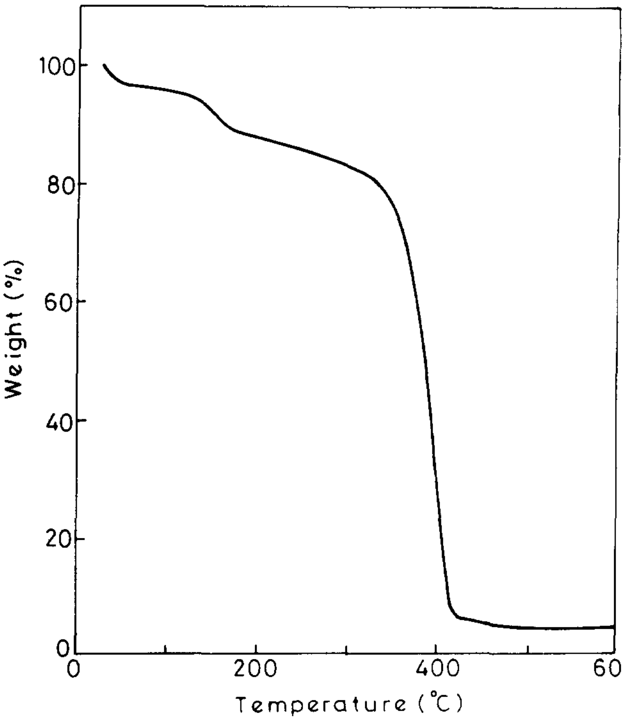

Figure 5 T.g.a. curve of terpolymer

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REFERENCES

1 Furukawa, J., Iseda, Y., Haga, K. and Kataoka, N. *J. Polym. Sci.* 1970, **8**, 1147

2 Hirooka, M., Yabuchi, H., Kawasuwi, S. and Nakguchi, K. *J. Polym. Sci.* 1973, **11**, 1281

3 Samuel, R. H. and David, K. H. *J. Appl. Polym. Sci.* 1975, **19**, 2370

4 Simionescu, C. I. and Liga, A. *Rev. Roum. Chim.* 1977, **22**, 49

5 Kruglova, V. A., Kizhnyaev, V. N. and Antonovich, A. A. *Isv. Vyssh. Uchebn. Zaved Khim. Khim. Tekhnol.* 1981, **24**, 1012

6 Ghanem, N. A., Messiha, N. N., Ikladious, N. E. and Shaaban, A. F. *J. Appl. Polym. Sci.* 1981, **26**, 97

7 Ismaipov, A. G., Rasulov, N. S., Sadykhov, I. D. and Karaeva, S. G. *Azerb. Khim. Zh.* 1982, 74

8 Zyubin, B. A., Goldfein, M. D., Rafikou, E. A. and Stepukhovich, A. D. *Isv. Vyssh. Uchebn. Zaved Khim. Khim. Tekhnol.* 1984, **27**, 457

9 Shouji, I., Takanito, I. and Tamotsu, S. *Macromolecules* 1986, **19**, 1800

10 Kressler, J., Bieger, W., Horvath, B. and Schmidt-Naake, G. *J. Macromol. Sci., Chem. (A)* 1987, **24**(6), 681

11 Staudner, E., Kysela, G. and Bartus, J. *J. Macromol. Sci., Pure Appl. Chem. (A)* 1992, **29**(10), 885

12 Hill, D. J. T., O'Donnell, J. H. and Remphrey, L. *J. Macromol. Sci., Pure Appl. Chem. (A)* 1992, **29**(9), 813

13 Mahmoud, A. A., Shaaban, A. F. and Khalil, A. A. *Polym. Int.* 1992, **27**, 333

14 Kumar, P., Narain, D. and Srivastava, A. K. *Polym. Int.* 1993, **337**, 221

15 Shukla, P. and Srivastava, A. K. *J. Polym. Sci.* 1989, **27**, 3811

16 Shukla, P. and Srivastava, A. K. *Makromol. Chem., Rapid Commun.* 1989, **10**, 589

17 Shukla, P. and Srivastava, A. K. *Polym. Int.* 1991, **25**, 159

18 Sayyah, S. M., Bhagat, A. A., Sabry, A. I., Said, F. I. and El-Hamouty, S. H. *Acta Polym.* 1989, **39**(7), 399

19 Finemann, M. and Ross, S. D. *J. Polym. Sci.* 1950, **5**, 259

20 Skoog, D. A. 'Principles of Instrumental Analysis', HRW International Editions, CBS College Publishing, Japan, 1985, pp. 718–19