Asian Journal of Chemistry Vol. 20, No. 7 (2008), 5197-5202

1:1 Alternating Copolymerization of Schiff Bases with Electrophilic Monomers

R. ANNALAKSHMI* and R. KAVITHA
Department of Chemistry, Aarupadai Veedu Institute of Technology
Paiyanoor-603 104, India
E-mail: anuram79@yahoo.co.in

The spontaneous copolymerization of the two Schiff bases *p*-chlorobenzylidene-1-naphthylamine and *p*-methoxybenzylidene-1-naphthylamine with several electrophilic monomers such as succinicanhydride, acryl amide, methacrylic acid, acrylic acid was reported in detail and also characterize them by ^{1}H NMR and IR spectral studies.

Key Words: Schiff base, Copolymerization, Electrophilic monomers.

INTRODUCTION

The alternating copolymerization of a cyclic phosphorous compound 2-phenyl-1,3,2-dioxaphospholane with several electrophilic monomer[1-4] and also many substituted Schiff bases such as benzylidene-*m*-toludiene, benzylidene-1-naphthylamine with vinyl monomers were reported earlier[5-8].

In the present study, it is proposed to synthesis the following copolymers: (1) poly(*p*-chlorobenzylidene-1-naphthylamine-co-succinic anhydride) (2) poly(*p*-chlorobenzylidene-1-naphthylamine-co-methacrylic acid) (3) poly(*p*-methoxybenzylidene-1-naphthylamine-co-acrylamide) (4) poly-(*p*-methoxybenzylidene-1-naphthylamine-co-acrylic acid).

The physical properties of these polymers such as colour, relative solubilities, *etc.* are also determined. The inherent viscosity of these polymers were measured in DMF solvent to determine the molecular weight of polymers. The structure of the repeat unit of these polymers may be established by IR and ^{1}H NMR spectra.

EXPERIMENTAL

The nucleophilic monomer (*p*-chlorobenzylidene-1-naphthylamine) and the electrophilic monomer (succinic anhydride) in 1:1 mole ratio were added into a polymer tube containing 5 mL of acetonitrile together with hydroquinone monomethyl ether (0.1 g) in order to prevent radical polymerization. The tube was then sealed and kept at 70 ºC for 3 d in nitrogen atmosphere. The polymer (*p*-chlorobenzylidene-1-naphthylamine-co-succinic anhydride) was precipitated by adding diethyl ether and dried at 60 ºC.

Polymer such as *p*-methoxybenzylidene-1-naphthylamine-co-acrylamide is also prepared in the same way by taking *p*-methoxybenzylidene-1-naphthylamine as nucleophilic monomer and acrylamide as electrophilic monomer. Similarly other polymer, poly(*p*-chlorobenzylidene-1-naphthylamine-co-methacrylic acid) is prepared by taking *p*-chlorobenzylidene-1-naphthylamine while methacrylic acid, poly(*p*-methoxybenzylidene-1-naphthylamine-co-acrylic acid) is prepared by taking *p*-methoxybenzylidene-1-naphthylamine and acrylic acid.

The characterization of the polymers were done qualitatively and quantitatively by using IR (recorded in Perkin-Elmer model spectrometer), ^{1}H NMR (recorded in ECA 500 MHz, DELTA 2-NMR spectrometer), solubility (different solvents) and viscosity (Ubblhode viscometer).

RESULTS AND DISCUSSION

The degree of polymerization and molecular weight of the copolymers were obtained by viscosity measurements (Table-1). The colours of the synthesized polymers were completely different from those of the monomers. The physical characteristics of the synthesized four co-polymers are given in Table-2. The solubility data of the four alternating copolymers were determined in various solvents by dissolving about 30-40 mg of the sample in 1 mL of solvent (Table-2). The copolymers have almost the same solubility.

Spectral analysis of copolymer-I: ^{1}H NMR spectrum of the alternating copolymer shows signals at 1.2-1.3 δ, 3.4-3.6 δ and multiplets at 6.7-7.4 δ and 7.8-7.9 δ. The triplet at 1.2-1.3 δ is due to CH_2 protons in the -CH_2-CO-O-. The signals at 3.4-3.6 δ are attributed to the -CH_2 protons of the -N-CO-CH_2- group. The multiplets at 6.7-7.9 δ is assigned to the aromatic protons. The signals at 6.7-7.4 δ are due to the aromatic protons of the phenyl group and the signals at 7.8-7.9 δ are due to the aromatic protons of the naphthyl group.

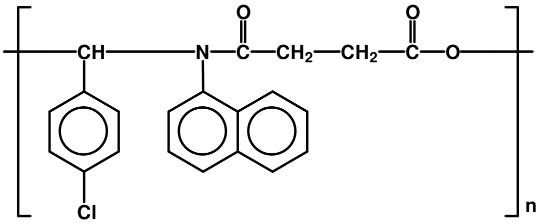
IR spectrum of the alternating copolymer shows characteristic absorption at 1178 cm^{-1} which is assigned to the -CO stretching frequency of the -COO group. The characteristic band at 1320 cm^{-1} is due to the -CN stretching frequency of the -CN group present in naphthyl ring.

The IR absorption band at 1394 cm^{-1} may be due to the aromatic C-C and C=C stretching vibrations.The absorption band at 1602 cm^{-1} is assigned to the -CO stretching frequency of the -N-CO group. The characteristic absorption at 1728 cm^{-1} is due to -CO stretching of the ester group. The absorption band at 3440-2839 cm^{-1} is due to aromatic C-H stretching vibrations and the absorption band at 1900 cm^{-1} may be attributed to the -C-Cl stretching of -Cl group attached to the benzene ring. The spectral data of copolymer I shows that it contains group from the Schiff base *p*-chlorobenzylidene-1-naphthylamine and -CO-CH_2-CH_2-CO-O- group of the succinic anhydride.

TABLE-1
SOLVENT: DIMETHYL FORMAMIDE

Concentration (g/dl)	η rel	η sp	η sp/c
Copolymer-I: (*p*-chlorobenzylidene-1-naphthylamine-co-succinic anhydride)			
1.000	1.160	0.160	0.160
0.833	1.124	0.124	0.148
0.714	1.100	0.100	0.140
0.625	1.084	0.084	0.134
0.555	1.048	0.048	0.086
Copolymer-II: (*p*-chlorobenzylidene-1-naphthylamine-co-methacrylic acid)			
1.000	1.170	0.170	0.170
0.833	1.132	0.132	0.158
0.714	1.105	0.105	0.147
0.625	1.086	0.086	0.137
0.555	1.051	0.051	0.091
Copolymer-III: (*p*-methoxybenzylidene-1-naphthylamine-co-acrylamide)			
1.000	1.198	0.198	0.198
0.833	1.150	0.150	0.180
0.714	1.122	0.122	0.171
0.625	1.102	0.102	0.163
0.555	1.065	0.065	0.117
Copolymer-IV: (*p*-methoxybenzylidene-1-naphthylamine-co-acrylic acid)			
1.000	1.186	0.186	0.186
0.833	1.142	0.142	0.170
0.714	1.133	0.133	0.159
0.625	1.071	0.071	0.113
0.555	1.045	0.045	0.097

Hence, the structure of copolymer I is assumed to be poly-(*p*-chlorobenzylidene-1-naphthylamine-co-succinic anhydride) and its structure is given as:



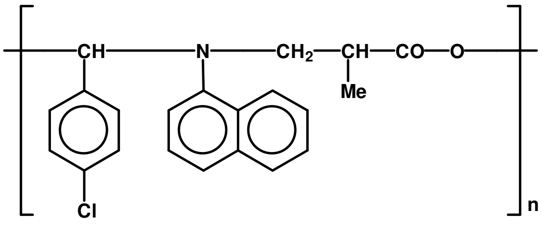
Spectral analysis of copolymer-II: ^{1}H NMR spectrum of the alternating copolymer shows signals at 1.2-1.4 δ, 3.4-3.6 δ, 4.2-4.9 δ, 6.2-6.4 δ and a multiplet at 6.7-7.4 δ and 7.6-8.1 δ. The signal at 1.2-1.4 δ is attributed

TABLE-2

Copolymer	Nature	Colour	Intrinsic viscosity	Solubility data	
				Solvents	Non-solvents
I	Gummy solid	Brownish black	0.092	Carbon tetrachloride, DMF, benzene, ether, 1,4-dioxane, DMSO	Diethylene glycol, water, cyclohexanol, methanol
II	Gummy solid	Brownish black	0.091	Carbon tetrachloride, DMF, benzene, ether, 1, 4dioxane, DMSO	Diethylene glycol, water, cyclohexanol, methanol
III	Gummy solid	Dark brown	0.101	Acetone, carbon tetrachloride, DMF, benzene, ether, 1,4-dioxane, DMSO	Isopropanol, chloroform, diethylene glycol, water, cyclohexanol, methanol
IV	Gummy solid	Brown	0.094	Acetone, carbon tetrachloride, DMF, benzene, ether, 1,4-dioxane, DMSO	Isopropanol, chloroform, diethylene glycol, water, cyclohexanol, methanol

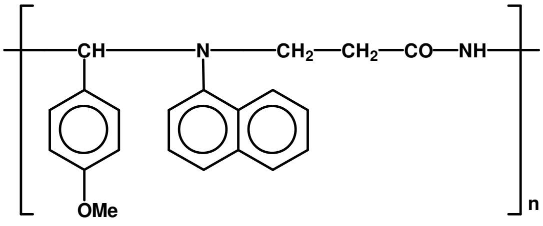
to the methyl protons of the $-CH(CH_3)-$ group. The signal at 3.4-3.6 δ is due to the $-CH_2$ protons of the $-CH_2-C(CH_3)-$ group. The multiplet at 4.2-4.9 δ may be due to -CH proton the $-CH_2-CH(CH_3)-$ group.The signal at 6.2-6.4 δ may be due to -CH protons of -CH-N- group. The multiplet at 6.7-7.4 δ is attributed to the aromatic protons of the phenyl group and the signals at 7.6-8.1 δ are assigned to the aromatic protons of the naphthyl group.

The absorption band of copolymer II at 820-750 cm^{-1} is due to the aromatic -CH bending vibrations. The absorption band at 1295 cm^{-1} may be due to CN stretching of N-naphthyl group. The IR band at 1450-1400 cm^{-1} may be assigned to the aromatic C-C and C=C stretching. The IR absorption band at 1903 cm^{-1} is due to the C-Cl stretching of Cl group attached to benzene The IR absorption band at 1690-1620 cm^{-1} is due to the -CO stretching of the ester group. The characteristic absorption at 3380-3050 cm^{-1} is assigned to the aromatic -CH stretching vibrations.The spectral data clearly indicates that the copolymer II contain group from the Schiff base (*p*-chlorobenzylidene-1-napthylamine) and $-CH_2-CH(CH_3)-COO-$ group of the methacrylic acid. Thus, the structure of copolymer II is assumed to be poly-(*p*-chlorobenzylidene-1-naphthylamine-co-methacrylic acid) and its structure is given as:



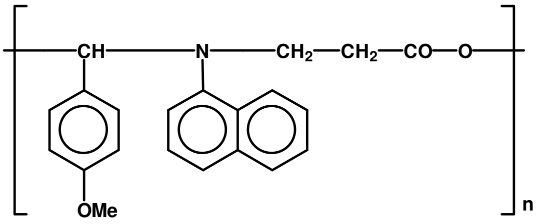
Spectral analysis of copolymer-III: ^{1}H NMR spectrum of the alternating copolymer shows signals at 1.2-1.9 δ, 2.7 δ, 3.7-3.9 δ, 5.5-5.8 δ, 6.1-6.2 δ and multiplets at 6.8-7.4 δ, 7.4-8.0 δ. The triplet at 1.5-1.9 δ is due to -CH_2 protons of the -CH_2-CO- group. The signal at 2.7 δ is attributed to the -CH_2(a) protons of-N-CH_2(a)-CH_2- group. The signal at 3.7-3.9 δ may be due to the CH_3-O- group present in the aromatic ring. The signal at 5.5-5.8 δ may be due to the -CH- proton of the -CH-N- group. The signal at 6.1-6.2 δ may be due to the -NH proton of the -CO-NH- group. The multiplet at 6.8-8.0 δ is assigned to the aromatic protons of the phenyl and naphthyl groups. The multiplet at 6.8-7.4 δ is attributed to the aromatic protons of the phenyl group and the signals at 7.4-8 δ are assigned to the aromatic protons of the naphthyl group.

The absorption band at 619 cm^{-1} is due to the aromatic C-N bending vibrations. The absorption band at 831-769 cm^{-1} is due to the aromatic C-H bending vibrations. The IR band at 1163 cm^{-1} may be assigned to C-N symmetric stretching vibrations. The absorption band at 1325 cm^{-1} is due to C-N stretching frequency of -CN group present in naphthyl ring. The IR band at 1423 cm^{-1} may be assigned to the aromatic C-C and C=C stretching. The absorption band at 1670 cm^{-1} may be due to -CO symmetric stretching of -CO-N- group. The IR band at 2931-2835 cm^{-1} is due to aliphatic -CH stretching frequency of -CH_2 group. The IR band at 3190 cm^{-1} is due to aromatic -CH stretching vibrations. The absorption band at 3355 cm^{-1} is due to the stretching frequency of the amide group. The spectral data clearly indicate that the copolymer III contains group from the Schiff bases (*p*-methoxybenzylidene-1-naphthylamine) and -CH_2-CH_2-CO-NH- group of the acrylamide. Hence, the structure of copolymer III is assumed to be poly-(*p*-methoxybenzylidene-1-naphthylamine-co-acrylamide) and its structure is given as:



Spectral analysis of copolymer-IV: ^{1}H NMR spectrum of the alternating copolymer shows signals at 1.2-1.4 δ, 2.6-2.8 δ, 3.7-3.9 δ, 5.5-5.7 δ and multiplets at 6.8-7.2 δ, 7.2-8.1 δ. The triplet at 1.2-1.4 δ may be due to -CH_2 protons of the -CH_2-COO-group. The signals at 2.6-2.8 δ is attributed to the -CH_2 protons of the -N-CH_2-CH_2- group. The signals at 3.7-3.9 δ may be due to the aromatic methoxy group. The signals at 5.5-5.7 δ may be due to -CH protons of the -CH-N- group. The multiplet at 6.8-8.1 δ is assigned to the aromatic protons of the phenyl and naphthyl groups. The multiplet at 6.8-7.2 δ is attributed to the aromatic protons of the phenyl group and the signals at 7.2-8.1 δ are assigned to the aromatic protons of the naphthyl groups.

The absorption band at 641 cm^{-1} is due to the aromatic -CN bending vibrations. The absorption band at 831-755 cm^{-1} may be due to aromatic -CH bending vibrations. The IR band at 1164 cm^{-1} is due to -CO symmetric stretching vibrations. The absorption band at 1249 cm^{-1} is due to -CO assymmetric stretching vibrations. The IR band at 1391-1302 cm^{-1} is due to -CN stretching frequency of N-naphthyl group. The absorption band at 1440-1422 cm^{-1} may be assigned to the aromatic C-C and C=C stretching. The absorption band at 1728 cm^{-1} is due to -CO symmetric stretching of ester group. The IR band at 2834 cm^{-1} is due to aliphatic -CH stretching of -CH_2 group. Thus, the spectral data clearly indicates that the copolymer IV contains group from the Schiff bases (*p*-methoxy benzylidene-1-naphthylamine) and -CH_2-CH_2-COO-group of the acrylic acid.Hence, the structure of copolymer IV is assumed to be poly-(*p*-methoxybenzylidene-1-naphthylamine-co-acrylic acid) and its structure is given as



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(*Received*: 18 June 2007; *Accepted*: 15 April 2008) AJC-6521