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Synthesis and Copolymerization Study of New Polyimide Precursors with Potential Application in Optical and Photonic Field

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New polyimide precursors were synthesized by simple one step procedure. (Z)-3-(4-Nitro-phenylcarbamoyl)-acrylic acid (A2), (Z)-3-(4-Ciano-phenylcarbamoyl)-acrylic acid (A3), (Z)-3-(4-Diethyl-phenylcarbamoyl)-acrylic acid (A4) and (Z)-3-[N′-(2,4-Dinitro-phenyl)-hydrazinocarbonyl]-acrylic acid (A6) were characterized by FT-IR, FT-NMR and UV-VIS spectroscopy. Test copolymerization successfully yielded copolymers that were characterized by FT-IR and FT-NMR spectroscopy. Improved solubility of these copolymers make them candidates for potential NLO applications.

Keywords: aniline derivatives; copolyimide; NLO potential; polyimide solubility

INTRODUCTION

Aromatic polyimides are known for their excellent thermooxidative stability, electrical properties and chemical resistance. Due to these characteristics such polymers are widely used in various applications [1–4]. However, most of the aromatic polyimides have more than one

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drawback, like their intractability in fully imidized form [5] or their insolubility in usual solvents, sources of major difficulties in processing. Therefore, the preparation of new monomers and redesigned soluble, thermoplastic copolyimides recently attracted great interest.

Using copolymerization as a method for improving the polymer properties represents an alternative way to overcome processing disadvantages and meet specific requirements.

Polymers with high nonlinear optical (NLO) properties are of major interest in developing electro-optic and photonic devices. In order to be useful in optical device applications, the synthesized materials should have a stable response at elevated temperatures and good chemical and physical stability as well [6].

In this article, four novel maleiamic monomers, (Z)-3-(4-Nitro-phenylcarbamoyl)-acrylic acid (A2), (Z)-3-(4-Ciano-phenylcarbamoyl)-acrylic acid (A3), (Z)-3-(4-Diethyl-phenylcarbamoyl)-acrylic acid (A4) and (Z)-3-[N′-(2,4-Dinitro-phenyl)-hydrazinocarbonyl]-acrylic acid (A6), were prepared from maleic anhydride with p-nitro-aniline, p-amino-bezonitrile, N,N-diethyl-p-amino-aniline and 2,4-dinitro-phenylhydrazine, respectively.

The article presents the synthesis and characterization of four new maleiamic monomers, the reactivity in radical copolymerization of (Z)-3-[N′-(2,4-Dinitro-phenyl)-hydrazinocarbonyl]-acrylic acid (A6) with styrene (St) and chloromethylstyrene (CMS) as well as the characterization of the obtained copolymers.

EXPERIMENTAL

Materials

Maleic anhydride (Aldrich) was recrystallized from chloroform. p-Amino-bezonitrile (Fluka, 97% pure), p-nitroaniline (Merck, for synthesis), N,N-diethyl p-aminoaniline (Fluka, purum), p-aminobenzoic acid (Merck, for synthesis) and 2,4-dinitrophenylhydrazine (Merck, for synthesis) were used as received. CMS (Aldrich) was used as supplied. St was purified by distillation under reduced pressure before using. AIBN (2,2′-azo-bis-isobutyronitrile, Aldrich) was recrystallized from methanol and benzoyl peroxide (PB, Aldrich) was used as supplied. Dimethyl formamide (DMF), dioxane, methanol (Merck, analytical grade) were dried according to standard procedure [7].

Measurements

The UV-VIS spectra for the monomers were taken in THF (thetrahydrofuran) with a Varian Carry 100 Spectrometer. ^{1}H-FT-NMR spectra

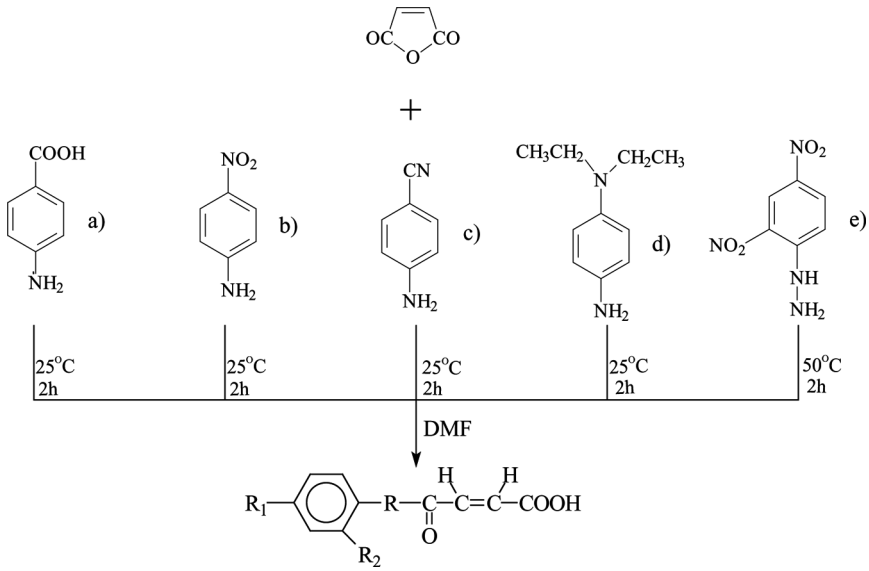
of monomers and copolymers samples were taken at 400 MHz and ^{13}C-FT-NMR spectra were recorded at 100 MHz in DMSO-d_6 (dimethyl sulfoxide) on a Varian Unity 400 Spectrometer. FT-IR spectra of monomers and copolymers samples were recorded on a Bruker Vertex 70 Spectrometer fitted with Harrick MVP 2 diamond ATR device.

Preparation of (Z)-3-(4-Carboxy-phenylcarbamoyl)-acrylic Acid (A1)

The A1 monomer was synthesized in a one step reaction from maleic anhydride and p-amino-benzoic acid (Scheme 1a) [8].

The solution of maleic anhydride (2.46 g, 0.025 mole) in DMF was gradually added while stirring, over a period of 10 min, to a solution of p-nitro-aniline (3.4 g, 0.025 mole) in DMF. The solution was stirred for 2 h at room temperature. The resulting solution was poured into crushed ice to precipitate crude A1. The crude A1 was filtered, dried and then recrystallized from methanol.

The FT-IR spectrum showed absorptions at 3500–2500 (carboxylic acid O–H), 3313, 1575, 1504 (amide N–H), 1682 (carboxylic acid and amide), 1289 (carboxylic acid C–O), 844 (CH=CH), 673 (C–H bending), all in cm^{-1}.



SCHEME 1 Synthetic route for the new monomers.

Preparation of (Z)-3-(4-Nitro-phenylcarbamoyl)-acrylic Acid (A2)

The A2 monomer was synthesized in a one step reaction from maleic anhydride and p-nitro-aniline (Scheme 1b). The procedure for sample A2 remains the same as before, maintaining the same molar ratio of 1:1 between the two reagents.

FT-IR: 3500-2500 (carboxylic acid O–H), 3293, 1547, 1510 (amide N–H), 1704 (carboxylic acid and amide), 1305 (carboxylic acid C–O), 849 (CH=CH), 685 (C–H bending), all in cm^{-1}.

Preparation of (Z)-3-(4-Ciano-phenylcarbamoyl)-acrylic Acid (A3)

The A3 monomer was synthesized in a one step reaction from maleic anhydride and p-amino benzonitril (Scheme 1c). The synthesis for monomer A3 was carried out under identical conditions as A1.

FT-IR: 3500-2500 (carboxylic acid O–H), 3330, 1492 (amide N–H), 1643 (carboxylic acid and amide), 1299 (carboxylic acid C–O), 855 (CH=CH), 617 (C–H bending), all in cm^{-1}.

Preparation of (Z)-3-(4-Diethyl-phenylcarbamoyl)-acrylic Acid (A4)

The A4 monomer was synthesized in a one step reaction from maleic anhydride and p-amino-N,N-diethyl-aniline (Scheme 1d). The procedure for sample A4 remains the same as before.

FT-IR: 3500-2500 (carboxylic acid O–H), 3275, 1514, 1464 (amide N–H), 1690 (carboxylic acid and amide), 1257 (carboxylic acid C–O), 844 (CH=CH), 619 (C–H bending), all in cm^{-1}.

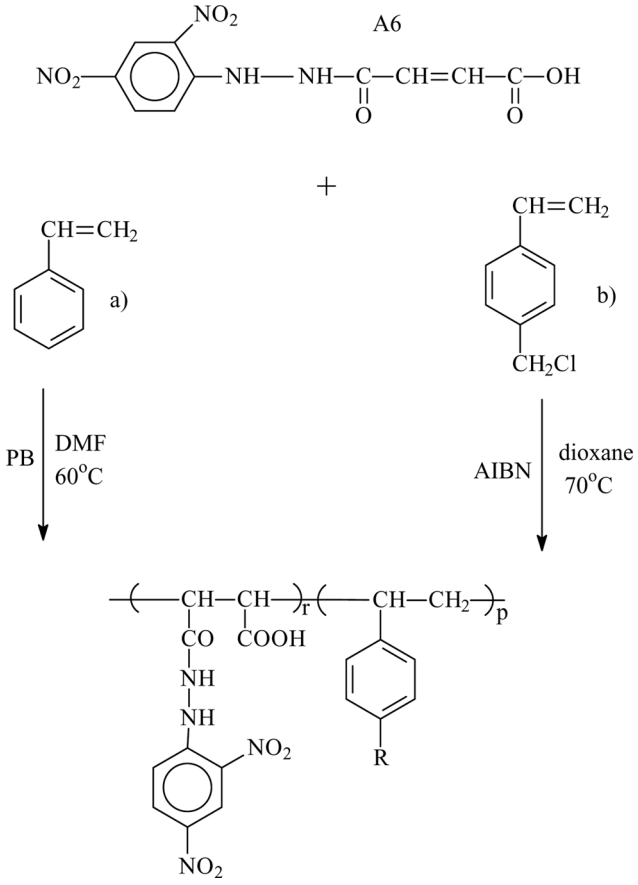
Preparation of (Z)-3-[N′-(2,4-Dinitro-phenyl)-hydrazinocarbonyl]-acrylic Acid (A6)

The A6 monomer was synthesized in a one step reaction from maleic anhydride and 2,4-dinitrophenylhydrazine (Scheme 1e). The procedure for sample A6 is the same, only this time the reaction is conducted at a temperature of 50°C.

FT-IR: 3500-2500 (carboxylic acid O–H), 3293, 1547, 1510 (amide N–H), 1704 (carboxylic acid and amide), 1305 (carboxylic acid C–O), 849 (CH=CH), 685 (C–H bending), all in cm^{-1}.

Copolymerization

The copolymerization of CMS and A6 was carried out at 70°C for 4 h in a round bottom flask with a reflux condenser, employing calculated amounts of comonomers in 50 ml dioxane with 0.0115 g AIBN (Scheme 2b). The 2nd copolymerization of St with A6 was performed in concentrated solution of DMF initiated with 0.0121 g of PB at 60°C for 4 h also (Scheme 2a). The copolymers were precipitated in methanol-petroleum ether mixture. After dissolving the crude copolymers in dioxane they were precipitated again in an excess quantity of methanol-water mixture. The purification process was repeated twice, and then the copolymers were dried at 60°C under vacuum for 48 h.



SCHEME 2 Synthetic route for the copolymers.

RESULTS AND DISCUSSION

Solubility Behaviour

All the synthesized monomers are soluble in acetone, dioxane, THF, DMF, DMSO; partially soluble in dichloromethane and chlorobenzene and insoluble in chloroform, ethyl ether, petroleum ether, at room temperature.

Spectral Characterization of Synthesized Monomers

All FT-IR and FT-NMR spectra (see Figs. 2–7) are supporting the structures of the monomers that we proposed. All NMR signals attributions are shown in Tables 2 and 3 for all the synthesized monomers. From the UV-VIS spectra (see Fig. 1) of the four novel monomers we calculate the molar extinction coefficients (ε) listed in Table 1.

Spectral Characterization for the Copolymers

The FT-IR spectra reveal the presence of absorption bands at 1872 and 1722 cm^{-1} due to stretching of C=O (ν_{CH}; ν_{COOH}) from the maleiamic ring of A6 in St-A6 copolymer, which confirms the gradual insertion of the maleiamic acid, (other characteristic vibrations are 694 cm^{-1}

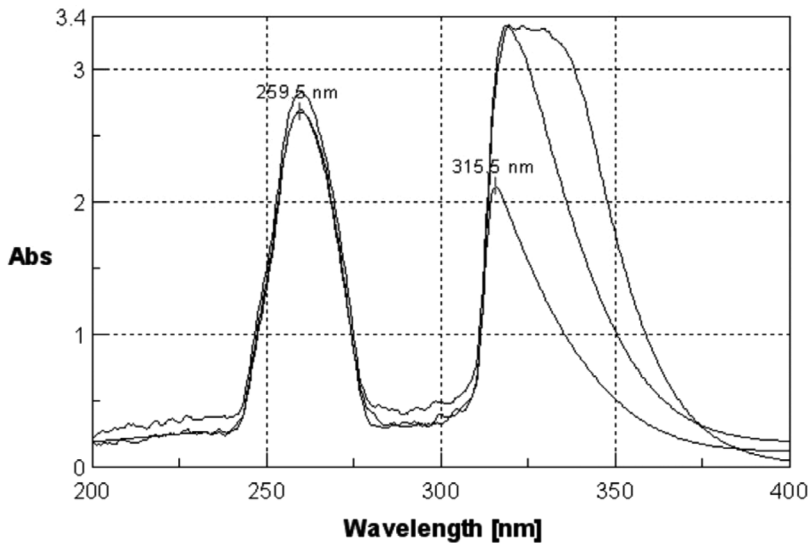


FIGURE 1 The UV-VIS spectra for A3 monomer.

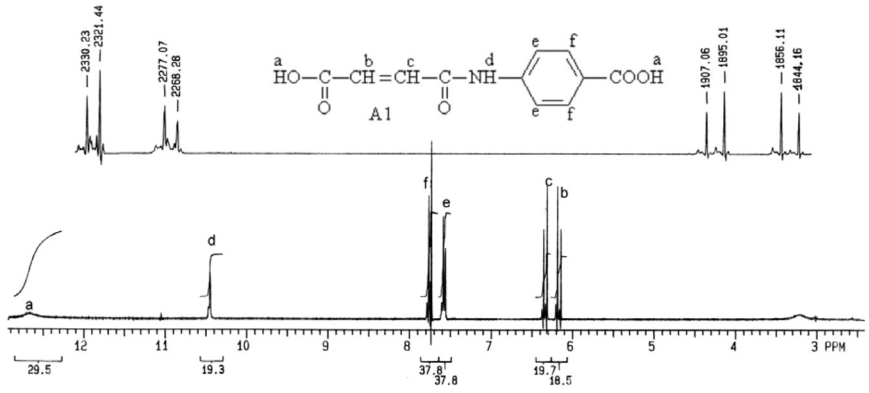


FIGURE 2 ^{1}H-FT-NMR spectra for A1 monomer.

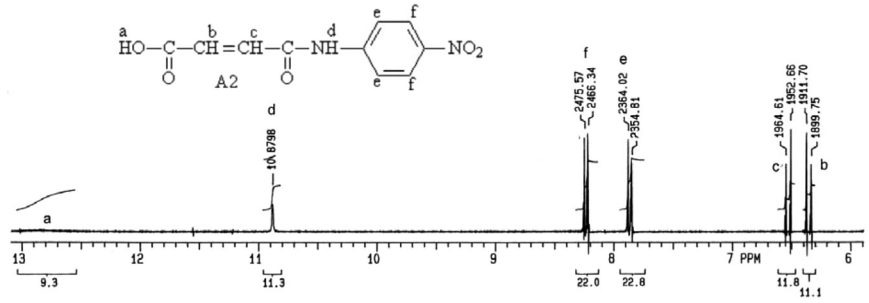


FIGURE 3 ^{1}H-FT-NMR spectra for A2 monomer.

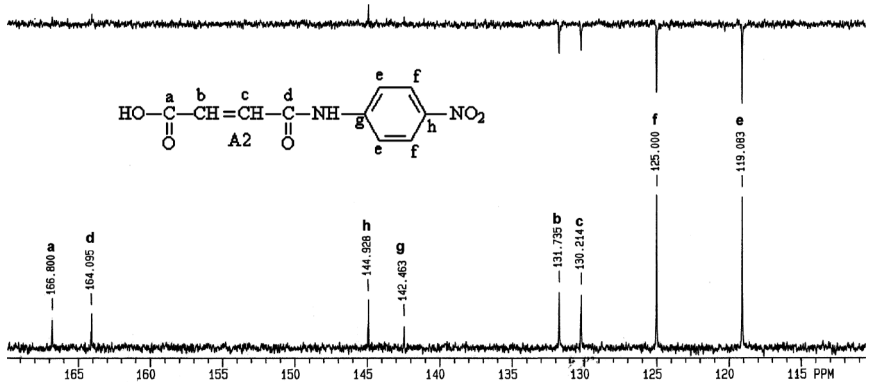


FIGURE 4 ^{13}C-FT-NMR spectra for A2 monomer.

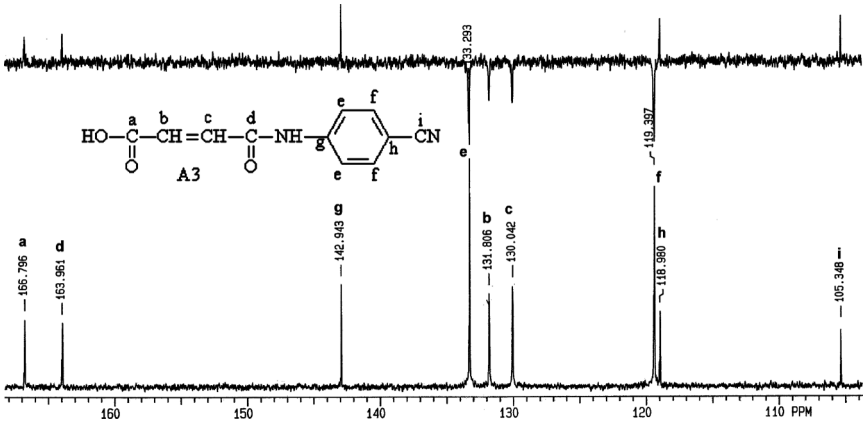


FIGURE 5 ^{13}C-FT-NMR spectra for A3 monomer.

(γ_{CH}), 2921 (ν_{CH} and ν_{NH}) and 2849 (ν_{CH})) as shown in Figure 8. CMS-A6 copolymer shows absorption bands at 1872 and 1722 cm^{-1}, and other important stretching bands can be observed at 1264 cm^{-1} (CH_2Cl), 3128–3026 cm^{-1} (ν_{CH}; ν_{COOH}), 2921 (ν_{CH} and ν_{NH}), 2849 (ν_{CH}).

From the ^{1}H-NMR spectra of the A6-CMS and A6-St copolymers, the A6 comonomer insertion could be evaluated, the molar ratio between the two comonomers depending on the reactive comonomer as follows: CMS/A6 = 1/0.45 and St/A6 = 1/0.2.

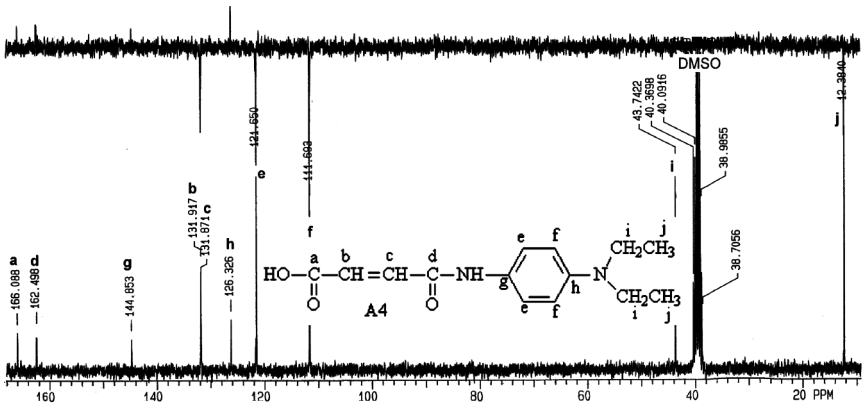


FIGURE 6 ^{13}C-FT-NMR spectra for A4 monomer.

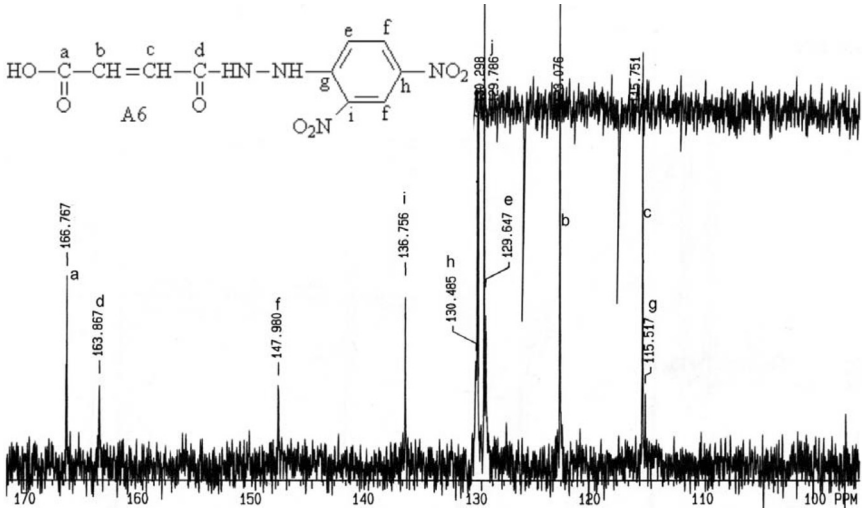


FIGURE 7 ^{13}C- FT-NMR spectra for A6 monomer

CONCLUSIONS

Four new monomers were synthesized and their structure was confirmed by FT-IR and FT-NMR spectra. The monomers showed excellent solubility in acetone, dioxane, THF, DMF and DMSO. Test radical copolymerization of (Z)-3-[N′-(2,4-Dinitro-phenyl)-hydrazino-carbonyl]-acrylic acid (A6) was successfully attempted with two different reactive comonomers. The copolymers were characterized

TABLE 1 Spectral and Physical Characteristics of the Synthesized Monomers

Monomer code	Yield (%)	Wave length (nm)	ε (l/mol cm)
A1	17	—	—
A2	34	260	88853
		358	8835
A3	52	259	8586
		315	155031
A4	28	260	25808
		319	25882
A6	85	261	54229
		454	59171

TABLE 2 ^{1}H-NMR Attributions for the Synthesized Monomers

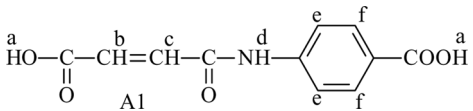
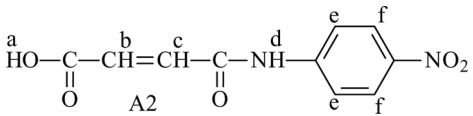
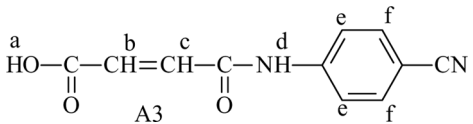
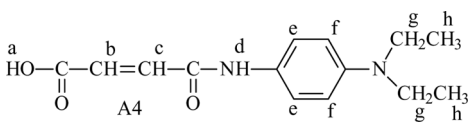
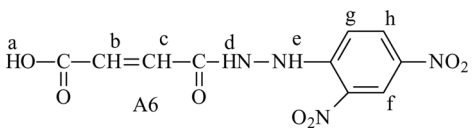
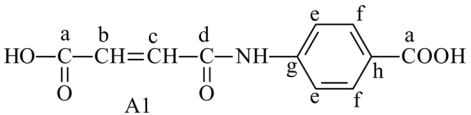
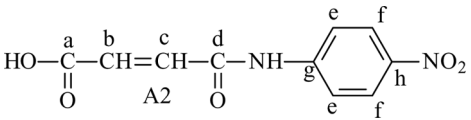
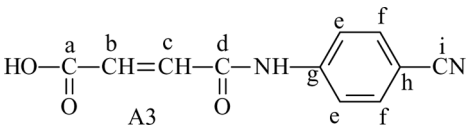
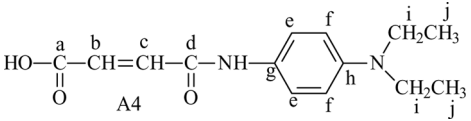
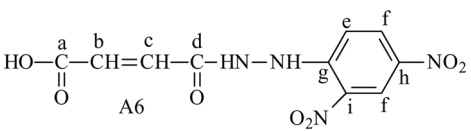
Compound	a	b	c	d	e	f	g	h
 A1	*s*, 2H, 12.65 ppm	*d*, 1H, 6.33 ppm	*d*, 1H, 6.16 ppm	*s*, 1H, 10.45 ppm	*d*, 2H, 7.57 ppm	*d*, 2H, 7.75 ppm	–	–
 A2	*s*, 1H, 12.8 ppm	*d*, 1H, 6.53 ppm	*d*, 1H, 6.35 ppm	*s*, 1H, 10.88 ppm	*d*, 2H, 8.23 ppm	*d*, 2H, 7.86 ppm	–	–
 A3	*s*, 1H, 12.4 ppm	*d*, 1H, 6.54 ppm	*d*, 1H, 6.36 ppm	*s*, 1H, 2.9 ppm	*d*, 2H, 7.82 ppm	*d*, 2H, 7.82 ppm	–	–
 A4	*s*, 1H, 12.3 ppm	*d*, 1H, 6.49 ppm	*d*, 1H, 6.28 ppm	*s*, 1H, 11.05 ppm	*d*, 2H, 7.43 ppm	*d*, 2H, 6.64 ppm	*q*, 4H, 3.31 ppm	*t*, 6H, 1.07 ppm
 A6	*s*, 1H, 12.5 ppm	*d*, 1H, 6.45 ppm	*d*, 1H, 6.33 ppm	*s*, 2H, 10.2 ppm		*d*, 1H, 8.86 ppm	*d*, 1H, 7.47 ppm	*dd*, 1H, 8.27 ppm

TABLE 3 ^{13}C-NMR Attributions for the Synthesized Monomers

Compound	a	b	c	d	e	f	g	h	i	j
 A1	166.9 ppm	131.7 ppm	130.2 ppm	163.6 ppm	130.4 ppm	118.7 ppm	142.7 ppm	125.6 ppm	–	–
 A2	166.8 ppm	131.7 ppm	130.2 ppm	164.1 ppm	119.1 ppm	125 ppm	142.5 ppm	144.9 ppm	–	–
 A3	166.8 ppm	131.8 ppm	130.0 ppm	164 ppm	133.3 ppm	119.4 ppm	142.9 ppm	118.9 ppm	105.3 ppm	–
 A4	166.1 ppm	131.9 ppm	131.8 ppm	162.5 ppm	121.6 ppm	111.7 ppm	144.8 ppm	126.3 ppm	43.7 ppm	12.4 ppm
 A6	176.8 ppm	123.1 ppm	115.7 ppm	163.8 ppm	129.7 ppm	130.3 ppm	147.9 ppm	136.7 ppm	166.7 ppm	130 ppm

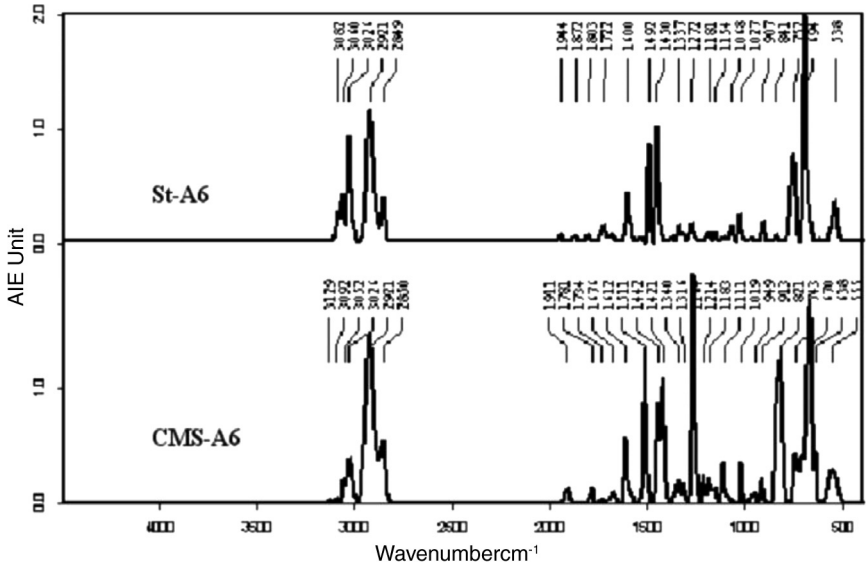


FIGURE 8 FT-IR spectra for the the synthesized copolymers.

by FT-IR and ^{1}H-FT-NMR spectroscopy. The successful insertion of synthesized compound in copolymer chain proves that these monomers can be used for designing materials with potential NLO applications.

REFERENCES

[1] Feger, C. J., Khojasteh, M. M., & McGrath, J. E. eds. (1989). *Polyimides: Materials, Chemistry and Characterization*, Elsevier Science Publishers: Amsterdam, Nederland.

[2] Lupinski, J. H. & Moore, R. S. (1989). *Polymeric Materials for Electronics Packaging and Interconnection*, American Chemical Society: Washington, U.S.A.

[3] Wilson, D., Stenzeberger, H. D., & Hergenrother, P. M. (1990). *Polyimide*, Chapt.7; Blackie: Glasgow, U.K.

[4] Scroog, C. E. (1976). *J. Polym. Sci. (Macromol. Rev.)*, *11*(1), 161–208.

[5] Mittal, K. L. Ed. (1984). *Synthesis, Characterization and Applications*, Plenum Press: New York, U.S.A., Vol. 1.

[6] Samyn, C., Verbiest, T., Kesters, E., Van den Broek, K., Van Beylen, M., & Persoons, A. (2000). *Polymer*, *41*, 6049–6054.

[7] Riddick, J. A., Bunger, W. B., & Sakano, T. K. (1986). *Organic Solvents Physical Properties and Methods of Purification*, Wiley Interscience: New York, U.S.A.

[8] Patel, C. B., Malek, N. I., & Oswal, S. L. (2006). *J. Macromol. Sci., Part A: Pure and Applied Chem.*, *303*, 43–289.