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POLY(MALEIC-AMIC) STRUCTURES FOR POTENTIAL NONLINEAR OPTICAL APPLICATIONS

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Noi structuri derivate de la copolimeri de metil metacrilat-anhidridă maleică şi clorometilstiren-anhidridă maleică au fost preparate prin reacţii polimer analoage cu diferite aniline. Aceşti copolimeri cât şi structurile lor derivate au fost caracterizate prin spectroscopie FT-IR şi analiza termogravimetrică DSC-TGA-MS. Copolimerii au fost de asemenea investigaţi prin spectroscopia de ^{1}H-RMN şi GPC. Deoarece structurile derivate preparate prezintă solubilitate excelentă în solveţii uzuali, aceşti polimeri devin candidaţi excelenţi pentru aplicaţiile NLO.

New structures were obtained from a one step condensation reaction of different derivatives of aniline with CMS-AM and MMA-AM copolymers. All samples were characterized by FT-IR spectroscopy and TGA-MS analysis.

CMS-AM and MMA-AM copolymers were also investigated by SEC and FT-NMR spectroscopy. Improved solubility of these structures make them candidates for potential NLO applications.

Keywords: maleic anhydride, functionalized copolymers, NLO.

1. Introduction

Nonlinear optical (NLO) materials have been in use for some time; now, a wide variety of such materials exist [1].

Since the last few decades, nonlinear optical (NLO) materials [2, 3] have drawn considerable research interest due to their potential commercial applications in optical communication, optical data storage, optical swithching and frequency modulation.

Recent research shows that most of the aromatic polyimides used in this field have more than one drawback such as their intractability in fully imidized

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form [4-6]. Due to their insolubility in usual solvents, difficulties in processing are encountered. Therefore, synthesis of soluble polymers having side chains maleimidic groups attracted high interest [7-9].

Using copolymerization [10, 11] as a method for improving the polymer properties represents an alternative way to overcome processing disadvantages and, at the same time, meet specific requirements.

In the present work, chloromethylstyrene–maleic anhydride copolymer (CMS-alt-AM) and methyl methacrylate–maleic anhydride copolymer (MMA-s-AM) were prepared from maleic anhydride with chloromethylstyrene and methyl methacrylate respectively by free radical copolymerization.

The paper presents the synthesis and characterization of MMA-AM and CMS-AM copolymers as well as of their functionalized derivatives.

The main interest of our work was to appreciate the evolution of each condensation reaction of different derivatives of aniline with synthesized MMA-AM and CMS-AM copolymers.

2. Experimental

Materials

Maleic anhydride (AM, Aldrich) was recrystallized from chloroform. 4-nitroaniline (pNA, Merck, for synthesis), 2-ciano-4nitroaniline (2CN4NA, Aldrich, for synthesis) 2,4-Dinitroaniline (DNA, Merck, for synthesis) and 6-chloro-2,4-Dinitroaniline (CLDNA, Merck, for synthesis) were used as such. Chloromethylstyrene (CMS, Aldrich) and methyl methacrylate (MMA, Aldrich) were freshly distilled under reduced pressure before use. AIBN (2,2′-azo-bis-isobutironitrile, Aldrich) was recrystallized from methanol and PB (benzoyl peroxide, Aldrich) was used as supplied. Dimethyl formamide (DMF), dioxane, toluene, methanol (all Merck, Analytical Grade) were dried and distilled according to standard procedures [12].

Characterization

^{1}H-FT-NMR spectra of investigated samples were taken in DMSO-d_6 (dimethyl sulfoxide) on a Varian Unity Spectrometer at 400 MHz. FT-IR spectra were recorded on a Bruker Vertex 70 Spectrometer fitted with Harrick MVP2 diamond ATR device. SEC (GPC) analyses were recorded with a Waters 410 endowed with Differential/ Refractometer /Waters 510/HPLC Pump. The thermal analysis (simultaneous TGA-DSC), MS hyphenated was performed on a STA 449C Jupiter NETZSCH/MS 403C Aëolas Mass Spectrometer.

Copolymerization of Methyl methacrylate / Maleic anhydride (MMA-AM)

The copolymer was prepared by free radical polymerization [13].
In 20 mL of toluene were dissolved 0.02 mol maleic anhydride and 0.03 mol methyl methacrylate (Figure 1.a), using AIBN (10^{-3} mol/l) as an initiator. The polymerization was allowed to continue for 2 h at 80°C. The resulting precipitate was mixed with fresh toluene and precipitated in petroleum ether. Yield: 75%. The product was purified twice by reprecipitation from acetone in petroleum ether and dried under vacuum for 48 h at 50 °C.

IR (ATR) ν: 1852 (C-O), 1778 (C=O) cm^{-1} due to carbonyl stretching in maleic anhydride ring and 1722 cm^{-1} (C=O) from MMA.

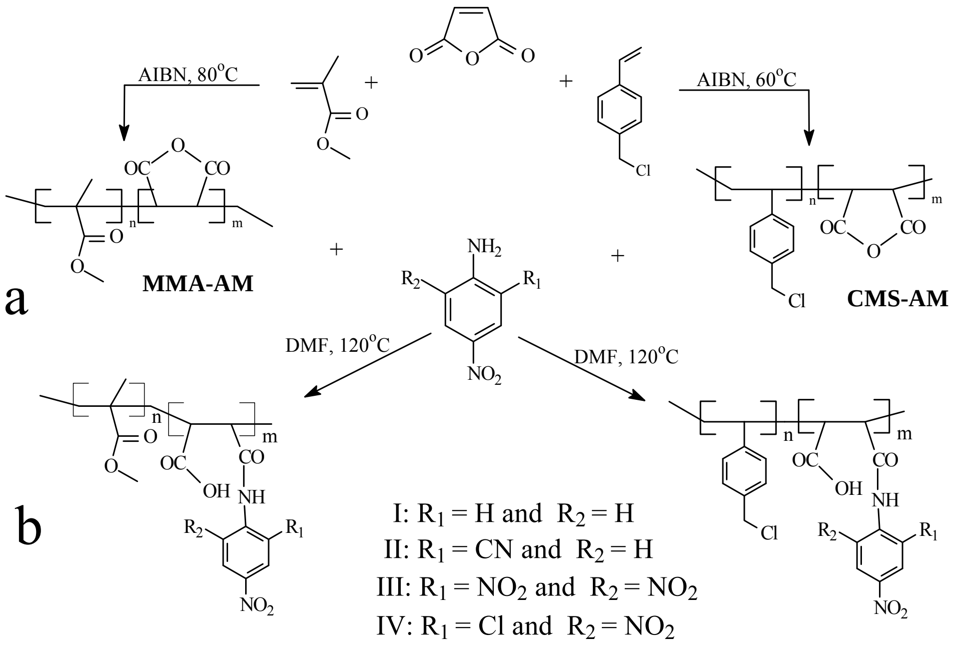

Fig 1: Copolymerization and functionalization

Copolymerization of Chloromethylstyrene and Maleic anhydride (CMS-AM)

This copolymer was also prepared by free radical polymerization [14] in 20 mL of toluene from 0.02 mol maleic anhydride and 0.02 mol chloromethylstyrene (Figure 1.a), using AIBN (10^{-3} mol/l) as an initiator.

CMS was gradually added, while stirring, to the maleic anhydride solution. The polymerization was carried out for 6 h at 60 °C. The crude precipitate was washed several times with toluene and dried for 24 h at 50 °C under vacuum. Yield: 85%. The product was purified twice by reprecipitation from acetone in petroleum ether.

IR (ATR) ν: 1852 (C-O), 1778 (C=O) cm^{-1} due to carbonyl stretching in maleic anhydride ring, 3035 (CH) and 1219 (CH_2-Cl) cm^{-1} (see also Figure 2).

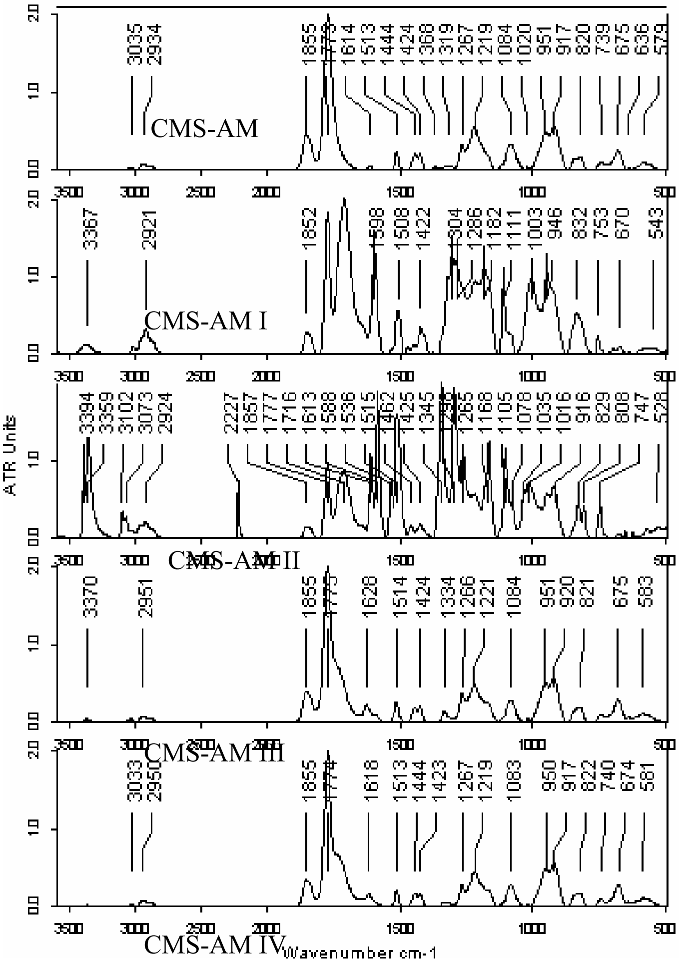

Fig 2: The FT-IR spectra for CMS-AM, CMS-AM I, CMS-AM II, CMS-AM III and CMS-AM IV

Based on SEC analysis we were able to calculate the exact amount of copolymers used in the next reaction (table 1).

Table1

SEC data for MMA-AM and CMS-AM copolymers

Code	Mn (dalton)	Mw (dalton)	Mz (dalton)	Id
MMA-AM	19359	37466	62434	1.94
CMS-AM	12330	32763	53350	2.66

Synthesis of functionalized copolymers derivated from MMA-AM / CMS-AM copolymers

The condensation reactions [15] between MMA-AM or CMS-AM copolymers and pNA, 2CN4NA, DNA and CLDNA were carried out at 120 ^{o}C for 2 h. In a round bottom flask equiped with a vertical condenser were taken pre-established amounts of copolymers and anilines (exp: MMA-AM: DNA = 1: 3) in DMF. (Figure 1.b). The resulting products were isolated by removing the solvent using a rotary evaporator and dried. Yields: 80-95%.

All copolymers samples were dissolved in acetone and then precipitated in petroleum ether. This procedure was repeated twice for removal of unreacted aniline derivatives in each case and dried at 50^{o}C under vacuum for 48 h.

3. Results and Discussion

Solubility behavior

All the copolymer samples were tested in a number of solvents; they are soluble in acetone, dioxane, THF, DMF, DMSO; insoluble in toluene, ethyl ether, petroleum ether.

Spectral characterization for functionalized copolymers

FT-IR spectra reveal the presence of absorption bands at 1618-1620 cm^{-1} due to stretching of amic-imide sequence (ν_{CO} ;$\nu_{C\text{-}N}$) from ring opening of AM for MMA-AM (I÷IV) and CMS-AM (I÷IV) functionalized samples (see Figure 2), which confirms side-chain covalent bonding of anilines to the copolymer backbone. Stretching of carboxylic group (ν_{COOH}) at 3300-3400 cm^{-1} also indicates ring opening of AM, 2920-2950 (ν_{CH}) and 1590 (NO_2) all in cm^{-1}.

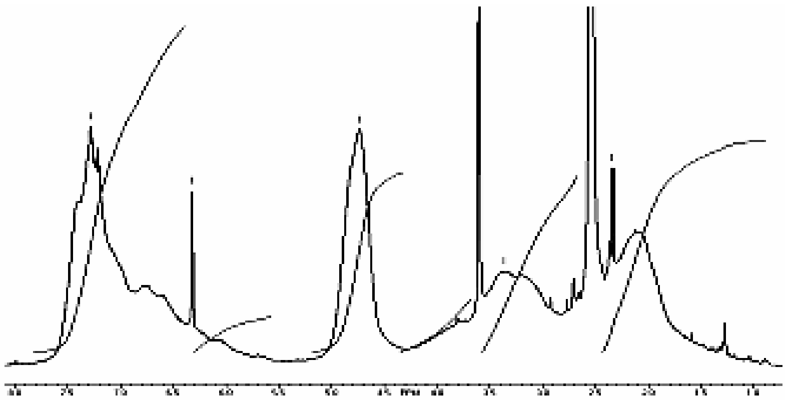

Fig 3: The ^{1}H-NMR spectra for CMS-AM copolymer

Spectral characterization of synthesized copolymers MMA-AM / CMS-AM

From ^{1}H-FT-NMR spectra we were able to calculate a molar ratio between units in copolymer as follows: MMA/AM = 2.05 and CMS/AM = 1.09.

CMS-AM copolymer: ^{1}H-NMR (DMSO-d_6): 7-7.5 ppm (aromatic protons), 4.5-5 ppm (CH_2-Cl protons), 3-3.5 ppm (-CH- from CMS-AM backbone) and 1.5-2.5 ppm (CH_2) (see also Figure 3).

MMA-AM copolymer: ^{1}H-NMR (DMSO-d_6): 4-4.5 ppm (-OCH_3 protons), 3-3.5 ppm (CH-CH protons from AM), 0.5-1 ppm (-CH_3) and 1.5-2 ppm (-CH_2- from MMA-AM backbone).

Thermal characterization of synthesized functionalized structures from MMA-AM / CMS-AM copolymers

For a better understanding of thermal behaviour of functionalized copolymers, some samples were investigated by DSC-TGA analysis (see table 2).

For every functionalized copolymer the TGA curve showed one more mass loss then the initial copolymer structure. This fact can be explained by aniline loss in each case.

The covalent bonding of anilines in copolymers side-chain can be noticed for MMA-AM functionalized samples only, by looking at Tg as shown in table 2. The functionalized copolymers exhibited an increase of Tg value with an increase in molecular weight. CMS-AM samples did not show any clear Tg.

Table 2

DSC-TGA parameters

CODE	*Tg (°C)*	*$T_{on\ set}$ (°C)*	*m (%)*			
			1st step	2nd step	3rd step	4th step
MMA-AM	77.3	83.2	8.38	85.33	-	-
MMA-AM III	125	120.5	0.39	2.62	88	-
MMA-AM IV	117.5	112.4	0.91	1.96	88.78	-
CMS-AM	-	-	9.63	28.46	36.43	-
CMS-AM III	-	-	5.02	22.65	22.47	17.09
CMS-AM IV	-	-	6.18	23.9	23.35	17.71

Thermal characterization of synthesized MMA-AM / CMS-AM copolymers

From the DSC curve it can be noticed that the MMA-AM copolymer shows a Tg situated at 83.2°C and on the other hand the CMS-AM copolymer does not present any clear Tg. MS signals recorded during TG analysis showed loss of CH_3 groups for MMA-AM copolymer, and loss of CH_2-Cl groups for CMS-AM copolymer after 130 °C, implying substituent cleavage.

Main chain destruction starts at 400°C for CMS-AM and at 290°C for MMA-AM respectively (see Figures 4 and 5).

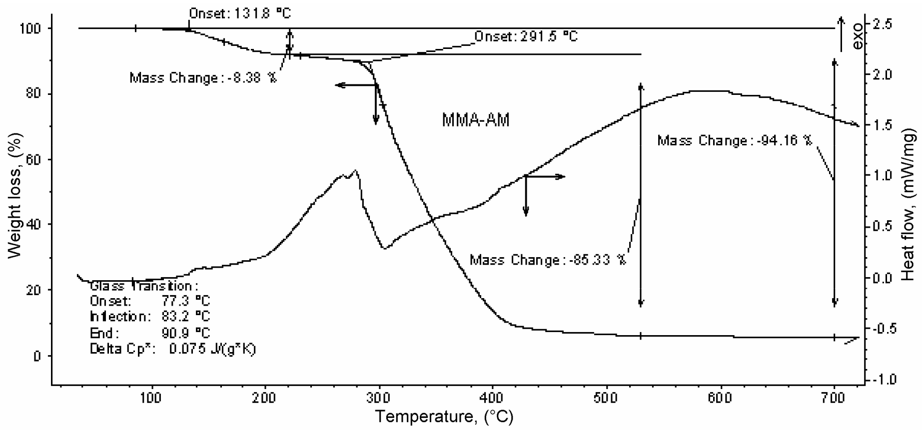

Fig 4: TGA-DSC thermogram for MMA-AM copolymer

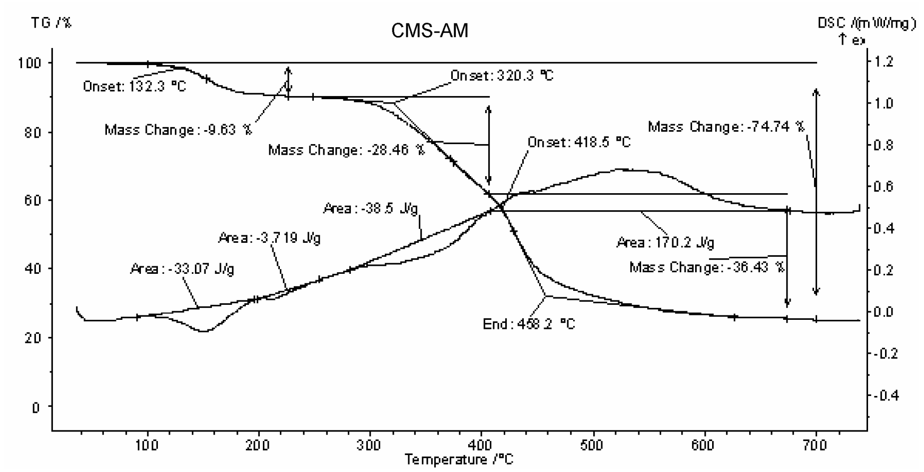

Figure 5: TGA-DSC thermogram for CMS-AM copolymer

4. Conclusions

New functionalized structures were synthesized with satisfactory yields and purity . The samples were investigated by FT-IR spectroscopy and DSC-TGA analysis. Functionalized copolymers show better thermal stability than the copolymers and excellent solubility in acetone, dioxane, THF, DMF, DMSO. Improved solubility of these functionalized copolymers structures make them proper candidates for potential NLO applications.

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