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Synthesis, Spectral and Thermal Characterization of Some Azo-Polymers Containing Acrylate Derivatives

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Research Article

ABSTRACT

A series of Azo-Acrylate Polymer derivatives have been synthesized via free radical polymerization by using initiator (azobisisobutyronitrile, AIBN) both conventional heating methods (CH) and Microwave irradiation method (MI). The spectroscopic and thermal characterizations of the polymers have been described by FT-IR, ^{1}H and ^{13}C-NMR, and TG/DTA. The molecular weights of polymers were determined by GPC. According to the result obtained from FT-IR spectra, C=O stretching vibrations of monomers increased in case of polymers as expected. It was seen from ^{13}C-NMR spectra that the shift of 10 ppm to the lower field relative to acryloyloxy azobenzene derivatives could be interpreted as a result of decreasing of electronic density around the carbon atom depending on the disappearance of the resonances of carbonyl group and ethylene group during the polymerization. Contrary to the Polydispersity Index (PDI) values in the polymers synthesized as using of CH method, the PDI values in the most of the polymers synthesized as using of MI method were lower.

INTRODUCTION

In the past two decades, due to having some benefits for practical photonic applications of materials relying on their outstanding processability, and low dielectric constants, Nonlinear Optical polymers (NLOPs) have drawn sustained concern [1]. Many organic chromophores having especially charming feature inherent exhibit photochromism, moreover, light can reversibly switch them between two different conformational expresses that exhibit distinct physical and spectroscopic characteristics [2]. Thus, not only is the task of the polymer matrix to provide a good film forming and thermomechanical features, but also it prevents excessive chromophore-chromophore interactions. Chromophore functions may be interdepended photochromism and photoluminescence features of the chromophore [3], or its nonlinear optical response [4,5]. Indeed, the nonlinear optics community has largely driven the quantitative understanding of the orientational order, structure-property relations and relaxation fact in the systems of polymer-chromophore, and this was later applied to analyze the photoinduced orientational mobility of azobenzene-including polymers [6,7].

Among the organic NLO molecules, intensive studies were focused on polymers including azobenzene (Azo-Polymers). It has been interested in Azo-dye chromophores by many researchers due to their relatively large molecular hyperpolorizability (β) and to delocalization of the π-electronic clouds [8-10]. Azo-polymers which are potentially functional materials for the applications such as optically driven machines, optical data storage, liquid crystal displays, polarization holography, and optical modulation, are known well as their isomerization influence trans and cis forms by irradiation of UV light and reserve process taking place as photochemical and/or thermal [11]. The reversible trans-cis isomerization of azobenzenes mainly focus on the photoresponsive behaviors of azo-

polymers such as surface relief grating formation, chromophore orientation, phase transition, and photomechanical bending. These photoresponsive variations of azo-polymers generally oriented perpendicularly to the polarization of the incident light through trans-cis-trans isomerization cycle that causes to crucial differences in their molecular shape and dipole moments [12,13].

It was demonstrated that the azo polymers photoresponsive features depend on the molecular structure such as types of azo chromophores, backbone chemical architecture, and positions to which azo chromophores were attached. In the research of azo polymers, synthesis and molecular design of azo polymers with different photoresponsive features become important [13]. Moreover, azo polymers have good mechanical features high chemical stability and great flexibility in manufacturing for the inter-chain bonded by covalent bonds [14]. In order to synthesize well-described low molecular weight polymers, Free Radical Polymerization (FRP) is one of the most appropriate methods in the existence of an aliphatic azo initiator azobisisobutyronitrile (AIBN).

Microwave irradiation (MI) might cause a decrease some organic reactions time, thus synthesis with microwave has been of enhancing concern to chemists. In comparison to conventional heating (CH), polymerization via microwave irradiation has a positive impact of higher reaction rates and higher monomer conversion in a shorter time. Namely, it may obviously increase the reactiveness of reaction system [15,16]. It has been synthesized in a research by Li et al. that 4-(4-methoxyphenyl-diazenyl) phenyl acrylate and 4-(4-nitrophenyldiazenyl) phenyl acrylate –P-NPAPA, consisting of azobenzene groups on the side chain by using atom transfer radical polymerization and free radical polymerization methods with both heating and microwave that are conventional. Furthermore, these phenyl acrylates are applied to a series of nonlinear optically (NLO) active homopolymers [15,17,18]. Nicolescu et al. studied spectroscopic methods to characterize some azobenzene methacrylate monomers [19] whereas these monomers also characterized by FTIR, ^{1}H-NMR, SEC and DSC-TGA methods [20]. The purpose of this study is to designed, synthesized a series of Azo-Polymers including acrylate derivatives **(Figure 1)** through free radical polymerization by using both conventional heating and microwave irradiation, and to characterize with spectroscopic methods and to determine their thermal properties.
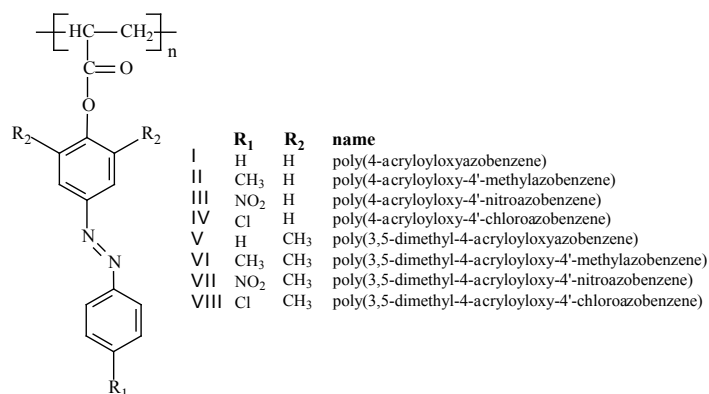

	R_1	R_2	name
I	H	H	poly(4-acryloyloxyazobenzene)
II	CH$_3$	H	poly(4-acryloyloxy-4'-methylazobenzene)
III	NO$_2$	H	poly(4-acryloyloxy-4'-nitroazobenzene)
IV	Cl	H	poly(4-acryloyloxy-4'-chloroazobenzene)
V	H	CH$_3$	poly(3,5-dimethyl-4-acryloyloxyazobenzene)
VI	CH$_3$	CH$_3$	poly(3,5-dimethyl-4-acryloyloxy-4'-methylazobenzene)
VII	NO$_2$	CH$_3$	poly(3,5-dimethyl-4-acryloyloxy-4'-nitroazobenzene)
VIII	Cl	CH$_3$	poly(3,5-dimethyl-4-acryloyloxy-4'-chloroazobenzene)

Figure 1. A series of azo-polymers containing acrylate derivatives.

EXPERIMENTAL

Materials

Aniline derivatives, acryloyl chloride and all solvents were purchased from commercial suppliers and used without purification. Azo compounds and their acrylate derivatives were synthesized similar to previously published procedure [21]. IR spectra were determined in the region 4000-200 cm^{-1} on a FTIR-8900 Schimadzu IR spectrometer by preparing samples as KBr pellets. The ^{1}H and ^{13}C-NMR spectra in DMSO-d$_6$ and CDCl$_3$ were measured at 200 and 50 MHz, respectively, with a Varian EM 360L NMR spectrometer using tetramethylsilane as internal standard. Thermal analyses were applied with a Perkin Elmer Diamond TG/DTA under dynamic nitrogen atmosphere at a heating rate of 10°C/min and at ambient temperature to 1000°C. α-Al$_2$O$_3$ was used as inert reference for DTA. The molecular weights of polymers were estimated by GPC with Agilent 1200 GPC and THF was used as the eluent.

Synthesis of azo-polymers

General procedures under microwave irradiation (MI): Polymerization process was implemented with free radical polymerization and it was used azobisisobutyronitrile as initiator. Household type microwave oven was used for the microwave irradiation. Polymerization reaction was applied as follows: a dry glass tube (10 mL) was filled with the mixture of 5 mmol azoacrylate monomer, 2.6 × 10^{-2} mmol initiator (azobisisobutyronitrile, AIBN) and 5 mL DMF as solvent. The reaction mixture was consecutively degassed through vacuum, charged with N$_2$ (five cycles), sealed under N$_2$, placed into a self-improved in-house microwave oven and refluxed within CCl$_4$ for an hour. This reaction was ended by immersing the tube in ice-water. After sufficient time, the reaction mixture was poured into a large excess of methanol. In order to remove unreacted monomer, the suspension was filtered. The obtained polymers were purified by precipitating from THF by adding of methanol and dried under vacuum at room temperature. The color and color codes of the resulting polymers are shown in **Table 1.**

Table 1. The color and color codes of the synthesized polymers.

Compound	Colour	Colour code	Compound	Colour	Colour code
I	Light brown	$S_{33}O_{70}Y_{60}$	V	Yellow-green	$S_{33}O_{41}Y_{70}$
II	Yellow	$S_{00}O_{20}Y_{99}$	VI	Brown	$S_{26}O_{99}Y_{60}$
III	Brown	$S_{41}O_{90}Y_{70}$	VII	Brown	$S_{70}O_{90}M_{07}$
IV	Brown	$S_{70}O_{80}Y_{33}$	VIII	Brown	$S_{80}O_{90}Y_{99}$

General procedures under conventional heating (CH): Polymerizations were performed in an oil bath held at 90°C. The other procedures are the same as those used for MI as explained in the previous section.

RESULTS AND DISCUSSION

FT-IR spectral analysis

IR vibrational frequencies of synthesized polymers are given in **Table 2** and the spectrum of poly(3,5-dimethyl-4-acryloyloxyazobenzene) (V) is shown in **Figure 2.** The assigned peak in the IR spectrum 1646-1631 cm^{-1} belonging to functional group $H_2C = CH-$ vibrations in acrylates series could not be observed in polymers of these compounds. Li et al. reported that IR spectrum of each polymer was similar to its monomer, and the absorption at 3080 and 1608 cm^{-1} which are attributed to C=C was weaken obviously, however carbonyl group absorption shifted to long wavelength due to disappearing the conjugation of carbonyl and ethenyl groups during the polymerization [16]. C=O stretching vibrations observed in the region 1747-1734 cm^{-1} in the spectra of monomers were shifted to 1755-1741 cm^{-1} in case of polymers. The shift was due to the disappearance of the conjugation with concomitant opening of ethenyl double bond. It could not be observed any C-H stretching peak in the region 3000-2800 cm^{-1} due to non-existence of aliphatic C-H groups in poly(4-acryloyloxyazobenzene) (I), poly(4-acryloyloxy-4'-methylazobenzene) (III) and poly(4-acryloyloxy-4'-chloroazobenzene) (IV) monomers while it was observed in the region 2935-2862 cm^{-1} in case of polymers and indicates the polymerization reaction occurred [21,22].

Table 2. Characteristic IR spectra of obtained polymers.

Compound	C-H	C=O	$-NO_2$, -Cl (para position)	C(O)-O-
(I)	2935-2862	1752		1145, 1194
(II)	2921-2850	1755	-	1151, 1195
(III)	2937	1752	1521, 1341	1132, 1191
(IV)	2926-2863	1754	1089	1147, 1175
(V)	2925-2862	1746	-	1170
(VI)	2922-2850	1748	-	1137
(VII)	2986	1741	1519, 1338	1191
(VIII)	2925-2963	1753	1089	1147
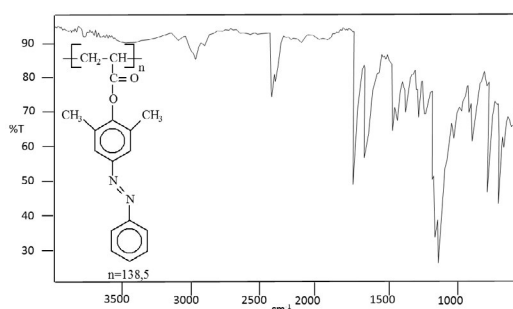
Figure 2. IR spectrum of Poly(3,5-dimethyl-4-acryloyloxyazobenzene) (V).

¹H-NMR spectral analysis

¹H-NMR spectra for polymers under study were obtained within solvents DMSO-d$_6$ or CDCl$_3$ and relative to tetramethylsilane (TMS). Types of protons, having different chemical environment present in the compounds, were determined through their different chemical shifts.

Methyl peaks belonging to DMSO-d$_6$ and water peaks in the solvent were observed at 2.49 ppm and 3.3 ppm, respectively [18]. Chemical shift values obtained from ¹H-NMR spectra for polymers under study are given in **Table 3.** Spectra of poly(4-acryloyloxy-4'-methylazobenzene) (II) and poly(3,5-dimethyl-4-acryloyloxyazobenzene) (V) are represented in **Figures 3 and 4** respectively.

Aromatic protons and aliphatic protons were observed in the range of 7.12 to 8.37 ppm and 1.18 to 3.75 ppm in the form of multiple and wide-band, respectively in the ¹H-NMR spectra of polymers. The lack of expected splitting for the CH-CH two protons in an orderly manner is due to structural variations by different chain length and nonlinearity leading to different chemical interaction of protons. The ethylenic protons of acryloyloxy azobenzene derivative in the range of 6.15 to 6.65 ppm were not

observed in their polymers, but the peaks observed in the range 1,18-3,75 ppm supports that C=C double bond was transformed into a C-C single bond and supports that polymerization occurs.

Table 3. ^{1}H-NMR values (in ppm) for polymers (t: triplet).

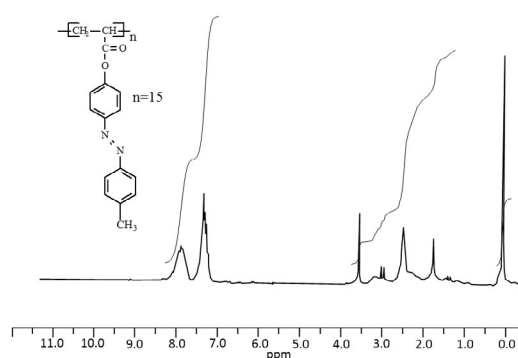| Compound	Aromatic protons	Ar-CH$_3$	-CH-CH$_2$-
(I)	7,24-7,72	-	1,22-3,17
(II)	7,27-8,09	2,49	1,76-3,56
(III)	7,32-8,37	-	1,25 (t); 1,86 (t); 3,75 (t)
(IV)	7,12-7,37	-	1,18-3,75
(V)	7,23-8,09	2,34-2,41	1,77-3,09
(VI)	7,15-7,28		1,67-2,43
(VII)	6,67-8,16	2,34	1,31-3,14
(VIII)	7,14-8,01	2,25	1,25-3,47

Figure 3. ^{1}H-NMR spectrum of poly(4-acryloyloxy-4'-methylazobenzene (II).
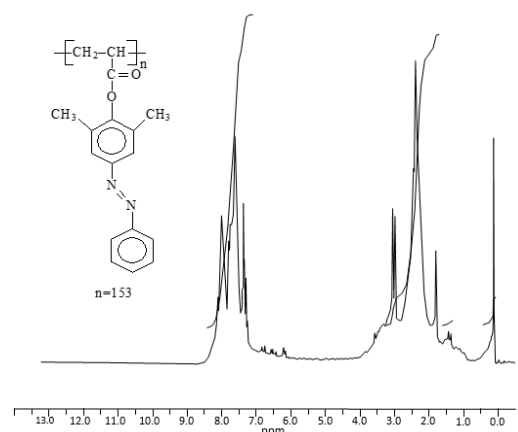

Figure 4. ^{1}H-NMR spectrum of poly(3,5-dimethyl-4-acryloyloxyazobenzene) (V).

^{13}C-NMR Spectral analysis

^{13}C-NMR spectra of polymers under study were obtained within solvents DMSO-d$_6$ or CDCl$_3$ relative to tetramethylsilane (TMS). Types of carbon atoms having different chemical environment present in the compounds were determined through their different chemical shifts. Because of the low abundance of ^{13}C isotope, spectrum must be taken in very high concentrations, but, in this case resolution problems arose. C peaks belonging to DMSO-d$_6$ were determined at 40 ppm as multiplet [23]. Chemical shifts obtained from ^{13}C-NMR spectra for synthesized polymers are given in **Table 4.**

Table 4. ^{13}C-NMR values (in ppm) for polymers.

Compounds	Observed signals
(I)	16,82; 40,30; 123,28; 123,99; 129,27; 130,97; 136,91; 150,05; 150,82; 172,50
(II)	21,50; 30,94; 42,60; 120,34; 122,13; 122,96; 123,96; 127,94; 129,66; 148,30; 149,02; 150,59; 151,95; 172,5
(III)	18,48; 25,66;58,50; 68,01; 122,51; 123,51; 124,79; 127,62; 133,35; 150,08; 153,74; 155,68; 164,06
(IV)	18,40; 25,59; 67,95;122,00; 124,10; 129,32; 137,10
(V)	17,03; 31,00; 36,50; 42,00; 120,40; 122,90; 123,15; 127,99; 129,13; 131,02; 148,50; 149,50; 172,20; 184,00
(VI)	16,97; 21,48; 30,96; 42,59; 120,35;122,86; 127,94; 129,70; 130,91; 142,00; 148,30; 149,02; 150,59; 151,00; 151,95; 172,00
(VII)	16,04; 29,72; 30,94; 31,48; 36,52; 42,60; 113,33; 120,03; 120,37; 126,37; 127,96; 128,55; 139,50; 148,33; 149,01; 152,21;152,92; 162,60

(VIII)	16,52; 16,94; 30,90; 31,13; 42,54; 120,30; 123,14; 123,31; 124,01; 127,89; 129,28; 131,03; 131,35; 136,90; 148,25; 148,96; 149,98; 150,05; 150,88; 150,97; 152,106; 172,06

The signals corresponding to carbon atoms of ethylene did not appear in the spectra of polymers. The signals of the carbon atom in carbonyl group appeared at 162.60-172.50 ppm. The shift of 10 ppm to the lower field relative to acryloyloxy azobenzene derivatives can be interpreted as a result of decreasing of electronic density around the carbon atom depending on the disappearance of the resonances of carbonyl group and ethylene group during the polymerization.

Although there were no signals in the region 10 to 50 ppm corresponding to the aliphatic carbon atoms in acryloyloxy azobenzene compounds except for methyl groups derivatives (I, III and IV), appearance of peak in the range 16.04-42.60 ppm in the synthesized polymers supported that the polymerization took place. More signals have been observed than the expected number of molecular formula in ^{13}C-NMR spectrum of the polymer. This is because a carbon atom located in the same position in different sizes of polymer molecules, may be related to having different chemical shifts in chains different lengths. ^{13}C-NMR spectra of the polymer II and V polymers were given in **Figures 5 and 6.** In some spectra were observed peaks not referring structure of polymers that we synthesized between 20-30 ppm. It is thought that these peaks result from not being completely dried of DMF used in the reactions.
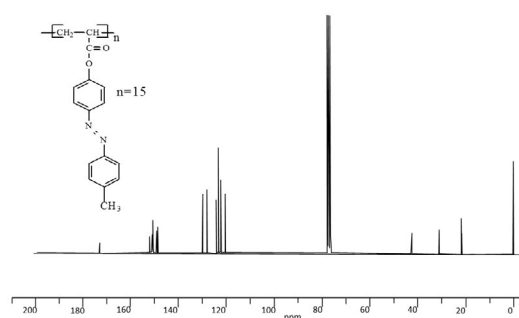

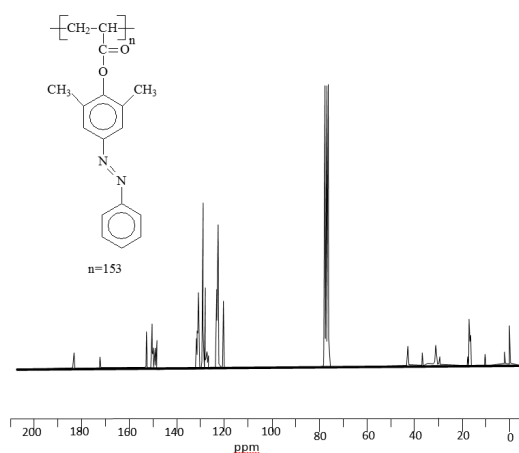**Figure 5.** ^{13}C-NMR spectrum of poly(4-acyloyloxy-4'-methylazobenzene) (II).

Figure 6. ^{13}C-NMR spectrum of poly(3,5-dimethyl-4-acyloyloxyazobenzene) (V).

Gel permeation chromatography

The Number of average molecular weight of the synthesized polymers were determined by GPC method. The analyses were performed by using an Agilent 1200 Series. Average molecular weight of polymer II obtained by conventional heating was found as 3406 g /mol while that of its counterpart synthesized by microwave was found as 4000 g/mol. In terms of the polymers that synthesized under MI, the polydispersity index (PDI) values that determined for the polymers I, II, III, VI and VII were lower than the value calculated for the polymers synthesized under CH and were more closer to the value of 1. Li et al. reported that molecular weight and PDI values for P-NPAPA polymer 2780 and 1.25, However we defined these values for polymer 3 as 3000, 1.12 for MI method and 2250, 1.30 for CH method [17]. Molecular weights and heterogeneous distribution values obtained from GPC diagram for polymers synthesized with microwave and traditional are presented in **Table 5.**

Table 5. Number-average molecular mass and PDI values of the polymer obtained by GPC.

Polymer	Number average molecular weight (MI)	Polydispersity index (PDI) i	Number average molecular weight (CH)	Polydispersity index (PDI)
(I)	3500	1,15	2720	1,41

(II)	4000	1,28	3406	1,56
(III)	3000	1,12	2250	1,30
(IV)	2700	1,07	2116	1,35
(V)	43000	1,14	4847	1,13
(VI)	2050	1,78	396	1,02
(VII)	735	1,12	3406	1,56
(VIII)	40000	1,25	4846	1,15

Thermal analysis

Thermal analyses of polymers were performed by heating up from ambient temperature to 1000°C, under a nitrogen atmosphere and heating rate is 30 to 35°C.

In some analysis, the low weight losses obtained around 150°C may be stemmed from DMF not being dried in polymers. Hence, these low weight losses were ignored. The thermal degradation is characterized by three stages as seen from the **Figures 7-10.** It was observed that the first degradation took place in the range 274-336°C and completely degraded to volatile species in examining thermograms of polymers obtained by thermal method. However, first degradation step took place in the range 258-350°C for the polymers III, V, VII completely decomposed into volatile species and others were degraded by losing weight in the range 87.28% to 97.88%. Synthesized polymers was submitted TG and differential analysis being thermally stable up to 226, 49, 207, 237, 230, 183, 48, 241 for heating method; 249, 233, 154, 240, 166, 224, 291, 221 for microwave method, respectively. Degradation of the compounds 2 and 7 at low temperature may be probably affected by the effects of humidity due to solvent evaporation.. It was seen polymers have higher thermal stability when compared with the thermal stability of their monomers [23].
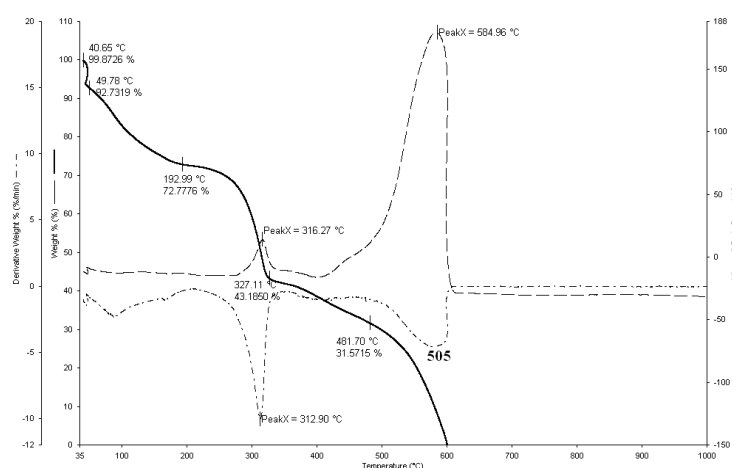

Figure 7. TG, DTG and DTA curves of poly(4-acyloyloxy-4'-methylazobenzene) (II) (obtained by CH).
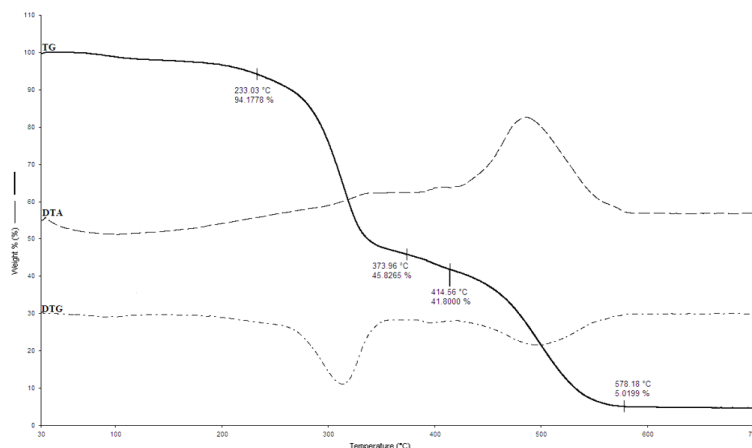

Figure 8. TG, DTG and DTA curves of poly(4-acyloyloxy-4'-methylazobenzene) (II) (obtained by MI).

The data related to thermal degradation are summarized in **Table 6.** Thermograms of the polymer II products obtained with the method of CH and MI is presented in **Figures 7 and 8** and also thermograms of polymer VIII products obtained both methods is given in **Figures 9 and 10.**
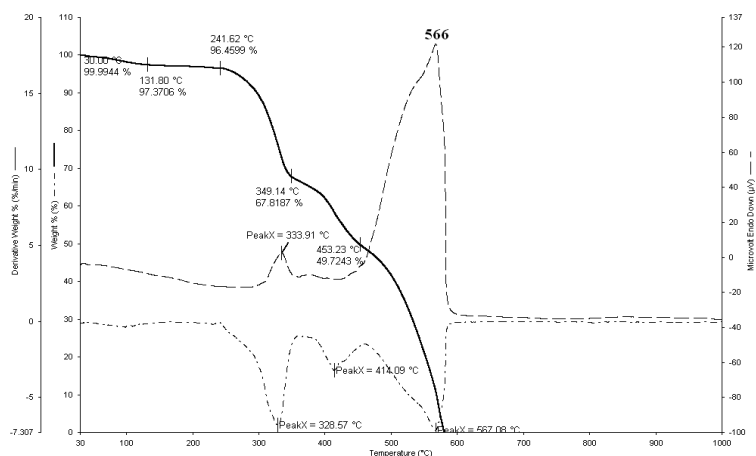
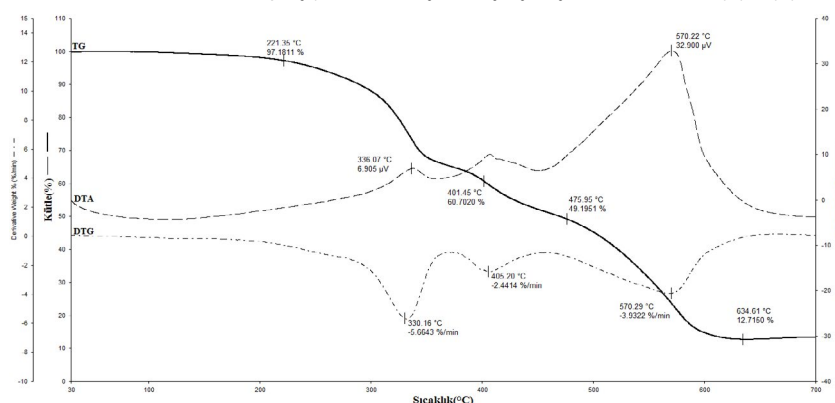**Figure 9.** TG, DTG and DTA curves of poly(3,5-dimethyl-4-acyloyloxy-4'-azobenzene) (VIII) (obtained by CH).

Figure 10. TG, DTG and DTA curves of poly(3,5-dimethyl-4-acyloyloxy-4'-azobenzene) (VIII) (obtained by MI).

Table 6. Thermal analysis value of polymers (in °C).

Polymer	Weight loss temperature rang	% Weight loss	Total weight loss %	DTA°C	DTG$_{max}$
I (heating)	30-343	48,08	48,08	327 exo	327
	343-502	22,16	66,24	546 exo	546
	502-600	33,76	100	589 exo	591
I (microwave)	30-372	36,4	36,43	328 exo	322
	372-446	13,51	49,94	450 exo	420
	446-612	40,10	90,04	533 exo	533
II (heating)	35-327	56,81	56,81	316 exo	313
	327-482	13,61	68,42	585 exo	505
	482-600	31,58	100		
II (microwave)	30-374	54,17	54,17	350 exo	320
	374-415	4,03	58,20	410 exo	395
	415-578	36,78	94,98	480 exo	480
III (heating)	30-207	11,43	11,43	209 endo	209
	207-399	36,62	48,05	274 exo	277
	399-600	51,95	100	529 exo	579
III (microwave)	30-330	74,64	74,64	258 exo	258
	330-398	12,23	86,87	380 exo	397
	398-611	13,13	100	466 exo	466
IV (heating)	30-334	43,73	43,73	328 exo	326
	334-469	12,69	56,42	599 exo	600
	469-600	43,58	100		
V (heating)	30-346	30,58	30,58		331
	346-384	3,20	33,78	336 exo	423
	384-469	19,14	52,92	547 exo	562
	469-613	46,13	99,05		
V (microwave)	30-404	46,90	46,90	330 exo	321
	404-481	22,13	69,03	450 exo	415
	481-583	31,97	100	520 exo	518

VI (microwave)	30-365	26,49	26,49	327 exo	316
	365-448	19,37	45,86	448 exo	422
	448-641	52,02	97,88	565 exo	562
VII (heating)	35-329	57,08	57,08	316 exo	313
	329-600	42,92	100	585 exo	505
VII (microwave)	30-375	26,06	26,06	333 exo	330
	375-535	67,80	93,86	490 exo	480
	535-545	6,14	100	545 exo	545
VIII (heating)	30-349	32,18	32,18	334 exo	328
	349-453	18,10	50,28	405 exo	414
	453-600	49,72	100	566 exo	567
VIII (microwave)	30-401	39,30	39,30	336 exo	330
	401-475	10,90	50,20	400 exo	405
	475-635	37,08	87,28	570 exo	570

CONCLUSION

This research may supply precious knowledge regarded synthesized polymers, focusing on some positive and negative features of it when choosing a specific monomer structure to design polymers. Hence, we have learnt that the number and the nature of the substituents might induce to different spectral and physical features. In this study, some Azo-polymers containing acrylate derivatives synthesized and structures of synthesized polymers by using under microwave irradiation and conventional heating methods with free-radical polymerization were determined as using of IR, ^{1}H-NMR and ^{13}C-NMR spectroscopies. Thermal behaviors of the compounds were studied by thermal analysis (TG/DTG/DTA). Three-stage mass loss was observed in general similar to margins for all polymers in the polymer thermal analysis studies.

Mn values from GPC for the polymers obtained by heating were found between 735 and 43000 g/mol, whereas they were found as 43.000 g/mol for the ones obtained from microwave irradiation. Molecular masses of polymers VII, I, II, III, IV, VI and VII were found as 3500, 4000, 3000, 2700, 2050 ve 735 g/mol, respectively. In generally, the PDI values determined for the most of the polymers synthesized under MI were lower than the value calculated for the polymers synthesized under CH and were closer to the value of 1.

The disappearance of the peak corresponding to the double bond in the IR spectrum and shifting to longer wavelengths of the absorption of carbonyl group due to the removal conjugation as a result of the opening of the double bond on Acryloyl group was confirmed that the polymerization reaction took place. This was also supported by ^{1}H-NMR and ^{13}C-NMR studies. The peaks belonging to C=C groups are not observed in these spectrums.

Consequently, microwave method may be said to be more efficient than thermal polymerization reaction in terms of obtaining higher molecular mass-polymers, polymerization taking place in a shorter time and synthesizing narrower molecular weight range.

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