NOVEL REACTIVE MONOMERS BEARING A PUSH-PULL AZO-MOIETY

Mitică Cezar SPIRIDON[1], Florica Adriana JERCA[2], Valentin Victor JERCA[3], Dumitru Mircea VULUGA[4], Dan Sorin VASILESCU[5]

In the present paper, we report the synthesis and characterization of two new reactive monomers bearing a push-pull azo-moiety, which are able to undergo homopolymerization. Promising azo-polymers for NLO applications are obtained with good yields. A comparison is carried between the reactivity of the azo-monomers, as well as between the corresponding azo-polymers, from the point of view of: solubility, molecular mass, glass transition temperatures, thermal stability, chromophore content, and spectral features.

Keywords: push-pull azobenzene, azo-monomer, homopolymer

1. Introduction

Today there is an ever-growing interest towards designing and developing new smart light-responsive azo-polymers.[1-3] This kind of macromolecular architecture receives tremendous attention in both fundamental and applied research areas,[4] mainly, on account of the reversible photoisomerization [2, 5] reaction of azobenzenes about the azo bond. The facile photoisomerization causes reversible changes of molecular properties (i.e. dipole moment, polarity, absorbance, etc.) and it's the key of some unique optical and photomechanical phenomena.[6, 7] Hence, azobenzene containing polymers find application as optical storage media,[8] liquid crystals polymers,[9] holographic memories,[10] photo-actuators,[11] nonlinear optical (NLO) materials,[12] etc.

It is widely acknowledged that the type of polymeric embedding matrix and azo dye, the nature of bonding between them, and the chromophore content play vital roles, when it comes for the final designed material to display certain photoinduced phenomena.[1, 13] Usually, an embedding matrix is chosen function of its film-forming ability, optical, thermal, and mechanical properties.[6, 13, 14] The

[1] Department of Polymer Science, University POLITEHNICA of Bucharest, Centre for Organic Chemistry Costin D. Nenitescu, Romanian Academy, Bucharest, Romania, e-mail: cezarspiridon@yahoo.co.uk
[2] Centre for Organic Chemistry Costin D. Nenitescu, Romanian Academy, Bucharest, Romania
[3] Centre for Organic Chemistry Costin D. Nenitescu, Romanian Academy, Bucharest, Romania
[4] Centre for Organic Chemistry Costin D. Nenitescu, Romanian Academy, Bucharest, Romania
[5] Department of Polymer Science, University POLITEHNICA of Bucharest, Romania

most encountered backbones, used as scaffolds for azo-moieties, include: methacrylates,[15] styrenes,[16] urethanes,[17] and imides[18] to name a few. Through the choice of suitable substituents, both the absorption spectrum of the chromophore and the kinetics of the isomerization reaction can be predicted. The most intensive studied azo dyes for NLO applications are those that have an aromatic ring substitution with electron-donor and -acceptor functional groups of appropriate strength.[13]

Between the polymer matrices and azo dyes can be established different bonding types, such as physical (i.e. guest-host systems), or chemical bonds.[1] It has been proven that covalent bonding is preferred for most applications, since it overcomes a series of inconveniences encountered at guest-host systems.[13] The free radical polymerization of azo-monomers is a well-known method used to design azo-polymers.[19] It is often used because of its simplicity, and more than that, it allows a facile and accurate control over the chromophore load.[20, 21] However, the low reactivity[20] of azo-monomers towards polymerization reaction (due to their bulkiness) and the high probability of chain transfer[22] are the major disadvantages that in most cases may lead to unsatisfactory results**.** To the best of our knowledge, the methacrylate-based monomers are capable to overcome easily such drawbacks,[23, 24] if certain aspects are to be tackled. Consequently, an azo-monomer should possess an optimal length of the flexible spacer that joints the azo moiety to the polymer backbone,[1, 13] since the dynamics of the side chain depends on the degrees of freedom of the azo groups, and has an impact on the overall optical properties of the final material.[8]

In the present paper, we report the synthesis and characterization of two reactive monomers bearing a push-pull azo-moiety, starting from a pseudo-stilbenes type azo dye. These azo-based methacrylate monomers are able to undergo free radical polymerization resulting polymers with the azo-moiety covalently linked through a flexible spacer to the backbone (see Fig. 1). All resulted structures are characterized by means of FT-IR, NMR spectroscopy and elemental analysis. The obtained homopolymers are also characterized by TGA and SEC analysis. Ultimately, a comparison is carried out between azo-monomers reactivity, as well as among the physical properties exhibited by the corresponding azo-polymers.

2. Experimental Section

2.1 Materials

N,N'-Dicyclohexyl carbodiimide (DCC, Aldrich), 4-dimethylamino pyridine (DMAP, Aldrich) and 2-hydroxymethyl methacrylate (HEMA, Merck) were used as received. Dry 1,4-dioxane and methylene chloride resulted after distillation over sodium metal wire. 2-Isopropenyl-2-oxazoline (IPRO, Aldrich)

was purified by low pressure distillation. N,N-Dimethylformamide (DMF) was dried over molecular sieves and 2,2-azo-bis(2-methylpropionitrile) (AIBN, Aldrich) was recrystallized from ethanol prior to use. 4-((4-(Diethylamino)phenyl)diazenyl) benzoic acid (D1) was synthesized according to reference.[25]

2.2. Characterization

FT-IR spectra were recorded on a Bruker Vertex 70 spectrometer fitted with a Harrick MVP2 diamond ATR device. NMR spectra were taken in $CDCl_3$ on a Varian Unity Spectrometer at 400 and 100 MHz at 30°C. The thermal analysis (simultaneous TGA–DSC, MS hyphenated) was performed on a NETZSCH STA 449C Jupiter system, coupled to an Aëolos II MS detector. TGA–DSC analysis was typically carried out from ambient temperature up to 720°C at a heating rate of 5°C/min, under helium gas flow. The number average molecular weights (Mn) have been evaluated by SEC with Wyatt Heleos II Multi Angle Light Scattering in-line and batch detector; using tetrahydrofuran as eluent (flow rate 1 mL/min), at 25 °C. The elemental analysis was carried out on a Costech ECS 4010 CHNS analyzer.

2.3. Synthesis

2.3.1 Monomer Synthesis

a) Synthesis of 2-methacrylamidoethyl 4-((4-(diethylamino) phenyl) diazenyl) benzoate (M1)

2.5 g (8.43 mmoles) of 4-((4-(diethylamino)phenyl)diazenyl) benzoic acid (D1) was dissolved in 20 mL of dried DMF, and then 0.7 mL (6.68 mmoles) of IPRO were added. The resulted mixture was subsequently left to react at 136 °C for 20 h. After completion, the solvent was removed by evaporation and the resulted solid was dissolved in benzene. The unreacted D1 was extracted after several washes with a 5% NaOH aqueous solution. After that, the azo-monomer solution was dried over anhydrous magnesium sulphate, and the benzene was separated by evaporation. The obtained product was dried overnight under vacuum at 80 °C. Yield: 91%. m.p. 133 °C.

^{1}H-NMR ($CDCl_3$, 30 °C) δ (ppm): 8.12 (d, 2H, *o*-ArH to COOR, J = 8.24 Hz), 7.86 (dd, 4H, *m*-ArH to COOR and *m*-ArH to NEt_2, J = 8.24 Hz and J = 9.7 Hz), 6.73 (d, 2H, *o*-ArH to NEt_2, J = 9.7 Hz,), 6.35 (s, 1H, NH), 5.71 (s, 1H), 5.34 (s, 1H), 4.49 (t, 2H, next to –OOC–Et), 3.73 (dd, 2H, next to –NHCO–Et), 3.47 (q, 4H, NEt_2), 1.97 (s, 3H), 1.12 (t, 6H, NEt_2). ^{13}C-NMR (100 MHz, $CDCl_3$, 30 °C) δ (ppm): 168.69 (ArC from –NHCO–), 166.8 (ArC from COOR), 156.49 (*p*-

ArC to COOR), 150.92 (ArC next to NEt_2), 143.34 (*p*-ArC to NEt_2), 139.85 (C from vinyl bond), 130.76 (*o*-ArCH to COOR), 129.45 (ArC next to COOR), 126.09 (*m*-ArCH to NEt_2), 122.11 (*m*-ArCH to COOR), 120.05 (CH_2 from vinyl bond), 111.12 (*o*-ArCH to NEt_2), 63.88 (–CH_2– next to –OOC–Ar), 44.92 (–CH_2 from NEt_2), 39.05 (–CH_2– next to –NHCO–Et), 18.75 (–CH_3 from vinyl bond), 12.79 (–CH_3 from NEt_2). Elem. Anal. calcd for $C_{23}H_{28}N_4O_3$: C 67.63, H 6.91, N 13.72, found: C 67.64, H 6.91, N 13.73.

b) Synthesis of 2-(methacryloyloxy)ethyl 4-((4-(diethylamino) phenyl) diazenyl) benzoate (M2)

A solution of 5 g (16.84 mmoles) of 4-((4-(diethylamino)phenyl)diazenyl) benzoic acid (D1) and 0.2057 g (1.684 mmoles) of DMAP in 42 mL of dry methylene chloride was prepared in advance. The mixture was placed in an ice bath, cooled to 0-5 °C until the dissolution of the reagents. A second solution of 3.4736 g (16.84 mmoles) DCC in 35 mL of methylene chloride was prepared and added dropwise over the first. Then, 2 mL (16.84 mmoles) of HEMA were mixed with 12.5 mL of methylene chloride and added in a similar manner over the resulted solution. After the complete addition of the third solution, the temperature was gradually increased up to room temperature and the reagents were left to react overnight under vigorous stirring.

The resulted by-product dicyclohexylurea (DHU) was separated from the mixture by filtration. The unreacted quantity of D1 was removed in a similar manner as in the case of M1. The solution containing M2 was dried over anhydrous $CaCl_2$ and the desired product was separated by evaporation of the solvent. The resulted quantity was dried overnight under vacuum at 60 °C. Yield: 93%. m.p. 74 °C.

^{1}H-NMR ($CDCl_3$, 30 °C) δ (ppm): 8.06 (d, 2H, *o*-ArH to COOR, J = 8.47 Hz), 7.78 (dd, 4H, *m*-ArH to COOR and *m*-ArH to NEt_2, J = 8.47 Hz and J = 9.12 Hz), 6.64(d, 2H, *o*-ArH to NEt_2, J = 9.12 Hz,), 6.08 (s, 1H), 5.51 (s, 1H), 4.5 (m, 2H, next to Ar –OOC–), 4.43 (m, 2H, next to -COOR), 3.38 (q, 4H, NEt_2), 1.88 (s, 3H), 1.15 (t, 6H, NEt_2). ^{13}C-NMR (100 MHz, $CDCl_3$, 30 °C) δ (ppm): 167.33(ArC from aromatic–COOR–), 166.23 (ArC from aliphatic COOR-), 156.41 (*p*-ArC to COOR), 150.86 (ArC next to NEt_2), 143.34 (*p*-ArC to NEt_2), 136.05 (C from vinyl bond), 130.77 (*o*-ArCH to COOR), 129.61 (ArC next to COOR), 126.29 (CH_2 from vinyl bond), 126.05 (*m*-ArCH to NEt_2), 122.06 (*m*-ArCH to COOR), 111.1 (*o*-ArCH to NEt_2), 62.8 (–CH_2– next to aromatic–COOR–), 62.56 (–CH_2– next to aliphatic COOR-), 44.91 (–CH_2 from NEt_2), 18.43 (–CH_3 from vinyl bond), 12.79 (–CH_3 from NEt_2). Elem. Anal. Calcd. for $C_{23}H_{27}N_3O_4$: C 67.46, H 6.65, N 10.26, found: C 67.47, H 6.65, N 10.26.

2.3.2. Polymer Synthesis

a) Synthesis of homopolymer P1

A 1M solution of 0.2035 g (0.5 mmoles) of M1 and AIBN (2% w/w to the monomer) in 0.5 mL of freshly distilled dioxane (dried and degassed) was prepared (Fig. 1). Then, the resulting mixture was sealed off in an ampoule, under argon cushion, and left to react over night at 80 °C. The solution was cooled down to room temperature, diluted with appox. 0.5 mL chloroform, and then the azo-polymer (P1) was separated by precipitation in ethyl ether. The obtained quantity was dried overnight under vacuum at 80 °C. Yield: 70%; Mn=4000 Da, PDI= 2.561.

^{1}H-NMR ($CDCl_3$, 30 °C) δ (ppm): 8.08 (2H, *o*-ArH to COOR), 7.81 (4H, *m*-ArH to COOR and *m*-ArH to NEt_2), 6.67 (2H, *o*-ArH to NEt_2), 4.35 (2H vicinal to ester group), 3.42 (2H vicinal to amide group overlap with C*H*$_2$ from N,N-diethyl), 1.5-2 (2H from backbone), 0.75-1.5 (3H from backbone overlap with C*H*$_3$ from N,N-diethyl).

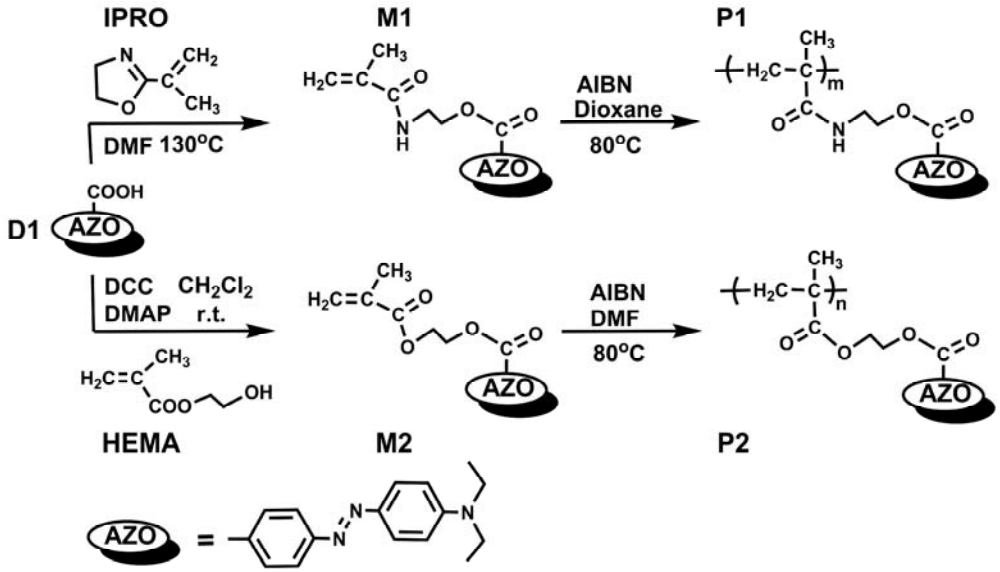

Fig 1. Synthesis routes for azo-monomers and the corresponding homopolymers

b) Synthesis of homopolymer P2

The homopolymer of M2 was synthesized under similar conditions; this time the quantities used were: 0.1 g (0.244 mmoles) of M2, AIBN (2% w/w to monomer) and 0.5 mL of DMF. The resulted polymer was separated by

precipitation in methanol, and dried in the same way. Yield: 75%, Mn=9200 Da, PDI=2.058.

^{1}H-NMR ($CDCl_3$, 30 °C) δ (ppm): 7.79 (2H, *o*-ArH to COOR), 7.71 (4H, *m*-ArH to COOR and *m*-ArH to NEt_2), 6.49 (2H, *o*-ArH to NEt_2), 4.26 (2H vicinal to aromatic ester group), 4.10 (2H vicinal to aliphatic ester group), 3.24-3.39 (4H from N,N-diethyl), 1.75-2 (2H from backbone), 0.75-1.25 (3H from backbone overlap with C*H*$_3$ from N,N-diethyl).

3. Results and Discussion

High reactive azo-monomers are demanded since through copolymerization, using particular co-monomers, the physical properties of the final materials can be easily tuned. Hence, azo-polymers with properties that meet specific requirements (i.e. enhanced film-forming ability, thermal stability, etc) can be obtained. The present study addresses an interesting approach to yield azo-monomers with high reactivity towards (co)polymerization, and in the same time to retain their optical features in future macromolecular structures.

First, a pseudo-stilbene type azo-dye, substituted with an electron-donor and an electron-acceptor group of appropriate strength, has been synthesized. Then, through the –COOH reactive groups of the chromophore, two new methacrylate-based monomers with similar structures are obtained with high yields. In the next stage, both azo-monomers easily undergo free radical homo-polymerization, under pre-established conditions.

The slight structural difference between M1 and M2 leads to significant changes of properties, i.e. difference in reactivity, which further affects the thermal stability of the corresponding homopolymers. The ester-amide/ester-ester formation acts as a flexible spacer that provides enhanced mobility of azo-moieties in future (co)polymers. Herein, all obtained structures are comparatively discussed in order to highlight the structure-property relationship.

3.1. FT-IR/ ^{1}H-NMR characterization

The chemical structure of the synthesized azo-monomers and their homopolymers (see Fig. 1) was confirmed by FT-IR and NMR spectroscopy. As it can be noticed in the recorded FT-IR spectra, presented in Fig. 2, the characteristic absorption bands of the ester groups present in both monomers (and polymers) can be found at: 1710 ($\nu_{C=O}$), 1265 (ν_{C-O-C}), and 1135 (ν_{C-O}) in cm^{-1}. The difference between the two monomers is easily pointed out by the appearance of characteristic absorption bands given by the amide groups from M1: $\nu_{C=O}$ at 1653 cm^{-1} and ν_{C-N} at 1514 cm^{-1}.

The formation of the homopolymers is more obvious in the ^{1}H-NMR spectra, as presented in Fig. 3. After the radical polymerization, the distinctive

signals of the vinyl groups from monomer M1 (at 5.71 and 5.34 ppm) and M2 (at 6.08 and 5.51 ppm) are shifted downfield under the backbone protons in the range of 1.5-2 ppm (in P1) and 1.75-2 ppm (in P2). The azo-moiety signals are found in each polymer spectrum at around 8.12-7.79, 7.86-7.71, and 6.73-6.49 ppm (aromatic protons), and at 1.12-1.15 ppm and 3.47-3.38 ppm show up the aliphatic protons of N,N-diethyl substituent.

In P1 spectrum, the signal from -CH_2- from N,N-diethyl overlaps with the signal given by the -CH_2- vicinal to the amide group at 3.42 ppm, and the signal given by the –CH_3 overlaps with the one from the backbone at around 0.75-1.5 ppm. In P2 spectrum, the situation changes and the signal given by -CH_2- vicinal to the aliphatic ester group overlaps with the one vicinal to aromatic ester group at 4-4.5 ppm. The spectral differences noticed between P1 and P2 are due to a slight change in structure from –NH- to -C=O-.

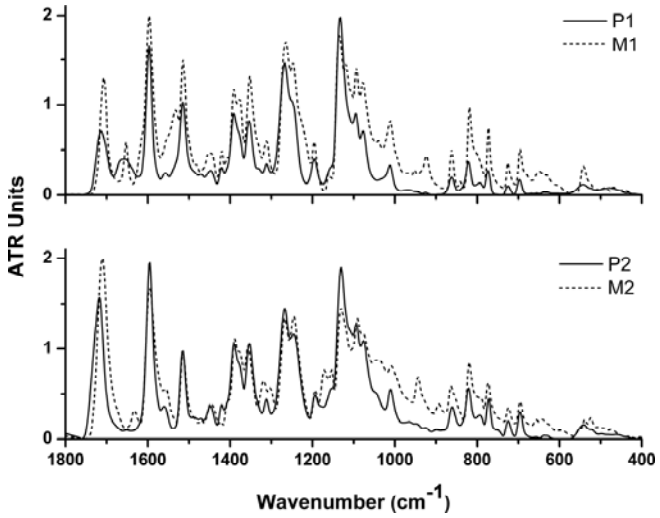

Fig. 2. FT-IR spectra of the azo-monomers and the corresponding homopolymers

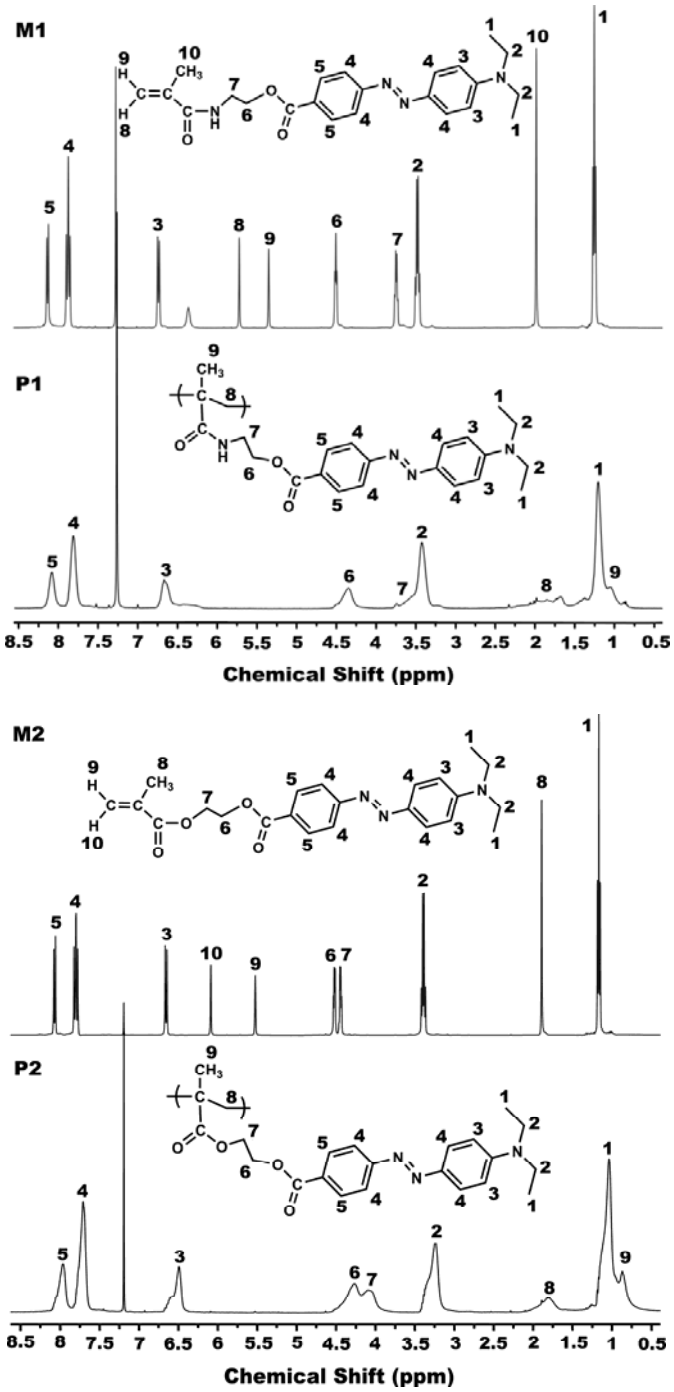

Fig 3. ^{1}H-NMR spectra for monomer M1 (up) and M2 (down) and their homopolymers

3.2. DSC-TGA characterization

The data provided from simultaneous TGA–DSC analysis for the two synthesized azo-homopolymers gives information about the structure-thermal properties relationship (i.e. T_g and thermal stability). These data are of interest since thermally stable materials are required for most of applications. Both homopolymers exhibit average glass transition temperature, 103.1°C for P1 and 108.9°C for P2, and attain good thermal stability since the T_d (temperature at 5% weight loss) value is 244.4°C for P1 and 294.6°C for P2. The slight difference in the T_g and T_d of these similar structures is on account of difference in their molecular weight. The tendency of M1 monomer to chain transfer is more pronounced, due to -NH- group; consequently a lower molecular mass was registered for its corresponding homopolymer P1. Therefore, higher molecular weights tend to increased thermal stability.

The thermograms obtained, given in Fig. 4, reveal that both P1 and P2 decompose in two stages. The weight loss is higher in the first stage due to the high content of azo-moiety. Enhanced thermal properties of polymers with such kind of azo-moiety should be attained after the azo-monomers are co-polymerized with proper co-monomers (i.e. styrene, 2-isopropenyl-2-oxazoline), so an optimum chromophore load could be chosen.

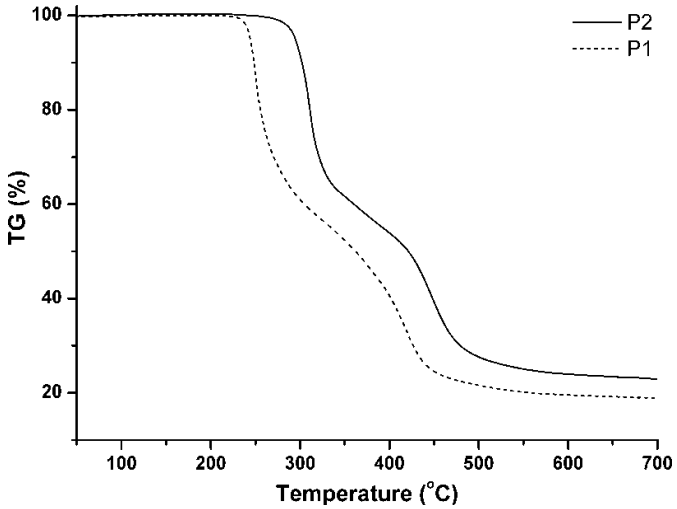

Fig. 4. TGA profiles for azo-polymers

4. Conclusions

Two new reactive monomers bearing a push-pull azo-moiety were synthesized and characterized. The increased reactivity of these azo-based methacrylate monomers was highlighted, since they undergo homopolymerization. The high reactivity ensures a promising degree of freedom for embedding this azo-moiety in various matrices, and through copolymerization, using particular co-monomers, the physical properties of the final materials can be easily tuned (i.e. enhancing the thermal properties, film-forming ability). This approach also facilitates the retaining of the push-pull character of the azo-moiety and the optical features in different polymer matrices.

All chemical structures were confirmed by means of FT-IR, NMR spectroscopy and elemental analysis. The SEC data revealed that the homopolymers have dissimilar number average molecular weights and polydispersity indices typical for free radical polymerization.

The thermal study revealed that both P1 and P2 exhibited average glass transition temperatures (T_g). Although, an optimum length of the flexible spacer is required to enhance dynamics of the azo-moiety in solid state-measurements, this feature seems to have a negative impact on the glass transition temperature. Nevertheless, the homopolymers evidenced good thermal stability, despite of all drawbacks mentioned earlier. However, this property may also be improved through copolymerization of the azo-monomers with particular co-monomers.

The comparison made between the two azo-monomers and related homopolymers allows us to have a better view over the relationship structure-properties of such compounds. This study pointed out that a synthesis strategy is in order as for an azo-monomer to possess high reactivity towards (co)polymerization, and in the same time to ensure certain features of future polymers. However, further studies (i.e. a solvatochromism study, isomerization kinetics) are demanded in order to gain insight into their photo-responsive behavior and their specific applications.

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