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ORIGINAL PAPER

Synthesis and characterization of side-chain poly(methacrylate)s bearing new azo-moieties

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Abstract New side-chain poly(methacrylate)s with azo moieties were prepared by free radical copolymerization, starting from methyl methacrylate (MMA) and some original azo-monomers. The chromophore content was evaluated from ^{1}H-NMR spectroscopy and elemental analyses; all structures exhibited a high content of azobenzene units. UV–Vis measurements have also supported this fact. Reactivity ratios for the methacrylate systems and their corresponding *Q*–*e* values were calculated based on several initial feed compositions (MMA and the newly synthesized azo-monomers) using an integral method with its appropriate software. The polymers were also characterized by FTIR, SEC and DSC-TGA techniques. The coloured poly(methacrylate)s exhibited glass transition temperatures between 141 and 168 °C and thermal stabilities up to 306 °C.

Keywords Azobenzene · Chromophores · Methyl methacrylate · Copolymers · Reactivity ratios · Side-chain moiety

Introduction

Azobenzene, with its two phenyl rings separated by an azo bond, acts as the parent structure for a broad class of aromatic azo compounds due to their versatility; accordingly, during the last decades, they have received much attention in both fundamental and applied research areas [1–3].

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One of the most interesting properties of these chromophores is the readily induced and reversible isomerisation of the azo bond between the more thermally stable *E* configuration and the *meta*-stable *Z* form [4]. Most azobenzenes can be optically isomerised from *E* to *Z* with light having the wavelength anywhere within the broad absorption band. The timescale of the thermal relaxation back into the *E* state is dictated by the substitution pattern. This "clean" photochemistry is the most important feature of azobenzene potential use as a tool for surface relief gratings (SRG) [5–9], or nonlinear optical (NLO) applications [10–12]. This light-induced inter-conversion allows systems incorporating azobenzenes to be used as photo-switches, and offers a reversible control over a variety of chemical, mechanical, electronic, and optical properties. Thus, the incorporation strategy is critical to exploiting azobenzene unique behaviour. One of the most attractive methods for incorporating azobenzene into functional materials is the covalent attachment to polymers. The resulting materials benefit from the inherent stability, rigidity, and processability of polymers, in addition to the unusual photo-responsive behaviour of the azo moieties.

Both side-chain and main-chain azobenzene polymers have been reported [12–19]. The reported synthetic strategies involve either the polymerization of azobenzene-functionalized monomers, or a polymer reaction, also called post-functionalization, which attaches an appropriate azo pendant group. Nonetheless, the first method is preferred for its simplicity and control of sequence distribution; the second takes advantage of commonly available starting materials, but may require more reaction steps. The numerous backbones used as scaffolds for azo moieties, include imides [20–22], esters [23–25], urethanes [26], or dendrimers [27]. The most common azo polymers are acrylates and methacrylates [28–33], due to their excellent film forming ability and good optical properties.

Our main purpose was to synthesize a range of side-chain poly(methacrylate)s bearing different azo-moieties with one or more substituents on the second aromatic ring and underline (by means of spectral and physical characterization) how the substitution pattern influences the copolymerization yields, the copolymers molar compositions and the final physical properties of each system. Therefore, this paper depicts the synthesis and characterization of new poly(methacrylate)s containing original azobenzene moieties prepared by free radical copolymerization. The synthesized polymers were characterized by FT-IR, UV–Vis, ^{1}H-NMR spectroscopy, by SEC and DSC-TGA techniques, and by elemental analysis. The copolymerization tests (using different molar feed ratios between comonomers) provided the necessary data for the calculation of the reactivity ratios and of the corresponding "*Q*–*e*" values.

Experimental

Materials

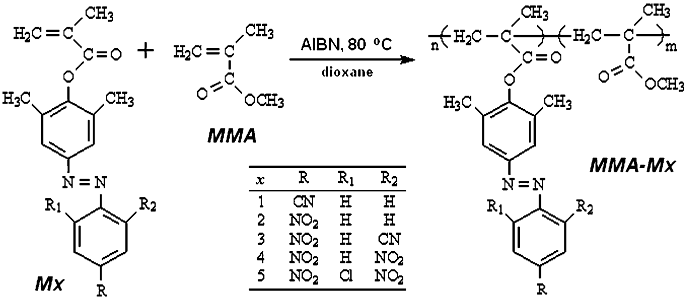
2,2′-Azobis(2-methylpropionitrile) (*AIBN*, Aldrich, 98%) was recrystalized from ethanol before use. Methyl methacrylate (MMA, Merck, for synthesis) was freshly distilled prior to use. The new methacrylate monomers with azobenzene moieties (Mx) have been prepared and purified according to the previously reported procedures [34]. Dioxane was distilled from CaH_2 before use.

Characterization

^{1}H-NMR spectra were taken in $CDCl_3$ on a Varian Unity Inova Spectrometer at 400 MHz. FT-IR spectra were recorded on a Bruker Vertex 70 Spectrometer fitted with Harrick MVP2 diamond ATR device. The elemental analysis was carried out by employing a Costech ECS 4010 CHNS analyzer. UV–Vis absorption spectra were acquired at 25 °C in dioxane with a Cintra 101 Spectrophotometer. The weight average molecular weights (M_w) of the copolymers were evaluated by SEC with Agilent 1200 Series Refractive Index Detector, (G1310A)-ISO HPLC Pump; using dimethylformamide as eluent (flow rate 1 mL/min), against polystyrene standards (six points from 10^2 to 10^6 Da). The thermal analysis (simultaneous TGA-DSC) was performed on a NETZSCH STA 449C Jupiter system. TGA-DSC for all the samples were typically carried out from ambient temperature up to 700 °C at a heating rate of 5 °C/min under helium gas flow.

Copolymerization

Five new coloured monomers (Mx) were copolymerized with MMA using different molar feed ratios between comonomers: MMA: Mx = 9:1, MMA: Mx = 8:2, and MMA: Mx = 7:3, respectively (see Scheme 1). The synthesis and characterization of Mx are described in Ref. [34]. A representative copolymerization procedure was as follows: 0.63 mmole of Mx and 1.47 mmole of MMA were taken in a vial. Then, *AIBN* (5×10^{-3} mol/L) and 1.5–2 mL of dry dioxane were added to prepare the final solutions (half lifetime of *AIBN* at 80 °C is approx. 1.5 h [35]). The resulting mixtures were well degassed and sealed off under argon cushion. The polymerizations were carried out at 80 °C for 21 h. After cooling down, the solutions were precipitated in 40 mL of diethyl ether. The copolymers were purified from unreacted monomers by reprecipitation from acetone in diethyl ether. The procedure



x	R	R_1	R_2
1	CN	H	H
2	NO_2	H	H
3	NO_2	H	CN
4	NO_2	H	NO_2
5	NO_2	Cl	NO_2

Scheme 1 Synthetic route for copolymers

was repeated twice for all 15 samples. The products were dried under vacuum at 70 °C for 48 h.

Results and discussion

All copolymers were obtained with good purities and yields. The samples were tested in a number of solvents, and showed an excellent solubility in polar solvents, such as $CHCl_3$, CH_2Cl_2, dichlorobenzene, dioxane, tetrahydrofuran, acetone, dimethylformamide, and dimethylsulfoxide.

The Mx were not able to homopolymerise through a radical mechanism, most likely due to their bulky substituents. Consequently, we tried to obtain binary copolymers with an adequate content of Mx units, (so that to be used in practical applications) choosing a related comonomer, namely MMA. The yields were strongly influenced by initial molar feeds; by increasing the Mx concentration in feed, a decrease of copolymerization yield and of molecular weight was recorded. The molecular weights obtained were high enough and all values are listed in Table 1 along with the corresponding polydispersity indices (PDI). This situation is drastically different from that reported by us [18] regarding the copolymerization of styrene with similar coloured monomers; in this last instance, the intense chain transfer severely limits the molecular weights. We noticed a decrease in the average molecular weights with the increase of azobenzene units in poly(methacrylate) compositions series. This behaviour was visible in all studied cases, no matter the nature (and number) of the substituents, and this was most certainly due to the same tendency towards chain transfer as previously reported [18]. We found that the polydispersity indices for MMA–M5 systems were not characteristic for free radical copolymerization; this system exhibited also the highest molecular weights.

The copolymer molar compositions were determined by two different methods, namely: elemental analysis and ^{1}H-NMR spectroscopy (see Table 1). The compositions given by elemental analysis were calculated on the basis of the nitrogen content, while the compositions given by ^{1}H-NMR spectroscopy were calculated based on the aromatic protons integral from azo-moieties against the methoxy protons integral from MMA. Since no other signals overlapped in the range of 7–8 and 3.5–4 ppm, we assume that the integrations were accurate. The values provided by these two methods of characterization were very similar; therefore, we consider the copolymer compositions reliable. Thus, the MMA–M2 systems exhibited the highest molar content in azo-moieties, closely followed by the MMA–M4 systems and finally the MMA–M5 systems included the lowest coloured monomer content. We can remark that the first two mentioned systems possess only $-NO_2$ substituents, but when a supplementary chlorine atom is introduced in the azo-moiety (MMA–M5) the azo content is drastically reduced.

The repeat units derived from Mx keep quasi-intact their optical properties in the final polymers. To validate this assertion, we measured the specific molar extinction coefficients (ε) of the repeat units derived from the Mx (see Table 2). Even if all specific molar extinctions coefficients are very high (and similar to those of the

Table 1 Physical data for MMA–Mx copolymers

System	MMA:Mx feed molar ratio	Y (%)	M_w ($\times 10^{-4}$ Da)	PDI	Cop. comp.[a]	Cop. comp.[b]	T_g (°C)	T_{onset} (°C)	Weight loss[c] (%)
MMA–M1	9:1	74	1.85	2.14	10.8	9.65	140.5	285	97.63
MMA–M1	8:2	50	1.36	2.07	5.6	4.77	152.3	280	93.37
MMA–M1	7:3	41	1.31	1.96	3.8	3.79	161.3	277	93.08
MMA–M2	9:1	59	2.78	2.16	9.2	8.2	141.9	306	89.87
MMA–M2	8:2	41	0.88	1.98	5	4.27	147.8	295	86.57
MMA–M2	7:3	38	0.59	1.95	3.2	3.4	152.7	291	80.96
MMA–M3	9:1	55	1.26	2.03	10.4	9.2	142	262	85.05
MMA–M3	8:2	42	0.93	1.72	5.4	4.9	147	258	74.62
MMA–M3	7:3	39.5	0.50	1.65	3.46	3.76	148	246	68.74
MMA–M4	9:1	43	2.10	2.08	9.43	9.76	141	281	91.15
MMA–M4	8:2	38	1.12	1.85	5.13	4.9	144.7	278	81.61
MMA–M4	7:3	36	0.54	1.76	3.64	3.65	146	272	75.77
MMA–M5	9:1	38	19.8	3.31	10.5	11.6	145.9	263	85.71
MMA–M5	8:2	32	14.9	3.03	6.67	7	164.8	252	66.4
MMA–M5	7:3	24	12.9	3.87	4.8	4.81	168.1	245	58.3

MMA/Mx molar composition: [a] given by ^{1}H-NMR, [b] given by elemental analysis; [c] at 700 °C

monomers Mx), they cannot be used in establishing copolymer compositions due to small irregular variations in the wavelength of maxima (λ_m).

In order to calculate the reactivity ratios, we used copolymer composition obtained from ^{1}H-NMR spectra. Our main concern was to achieve high conversions in copolymers of MMA with Mx so that to perform the corresponding tests; consequently the use of differential methods such as Fineman–Ross (FR), Kelen–Tüdös (KT), Yezrielev–Brokhina-Roskin (YBR) or Tidwell-Mortimer (TM) became out of question. To calculate reliable values, one has to employ integral methods; accordingly, we have used an appropriate method and software, namely the *OptPex2 program*, provided by Hagiopol et al. [36]. The results are presented in Table 3 and the values for r_2 sustain the fact that Mx do not homo-polymerize, but show a tendency to copolymerize with MMA. These values allowed us to calculate the corresponding "*Q*–*e*" values (see also Table 3); the high "*e*" values are attributable to the highly aromatic and polar substituents. Knowing that for MMA the corresponding "*e*" value is $e_1 = 0.4$, it becomes understandable why it is possible to insert important amounts of Mx in the copolymer chain. In addition, the r_2 value obtained for MMA–M2 system was much higher than the other ones, indicating that this particular monomer (M2) exhibits improved reactivity in copolymerization towards MMA. This result is in good agreement with the fact that MMA–M2 systems registered the highest molar composition in azo-moieties and increased molecular weights. Consequently, the MMA–M2 system also exhibited the highest thermal stability (see Table 1).

Table 2 UV data for Mx monomers and related MMA–Mx copolymers

UV data for monomers[a]			UV data for side-chain azobenzene units			
Mx	λ_m (nm)	ε (× 10^{-4} l/mol cm)	Y_2^b	Conc.[c] (g/l)	λ_m (nm)	ε (×10^{-4} l/mol cm)
M1	336	5.44	0.085	0.0568	333	5.55
			0.152	0.0344	333	4.36
			0.208	0.0288	334	5.33
M2	341	6.10	0.098	0.0780	344	3.86
			0.156	0.0392	344	4.40
			0.238	0.0156	345	5.82
M3	360	6.18	0.088	0.0296	360	6.71
			0.152	0.0428	360	5.77
			0.217	0.0200	360	5.96
M4	349	5.53	0.096	0.0648	349	5.32
			0.164	0.0504	349	5.79
			0.217	0.0456	346	5.43
M5	343	2.84	0.087	0.0568	340	3.61
			0.132	0.0473	340	3.27
			0.172	0.0592	340	4.90

[a] See also reference [34]

[b] Molar fraction of repeat units derived from monomers Mx, calculated from NMR data

[c] Solution in dioxane

Table 3 Reactivity ratios for MMA–Mx systems and their corresponding *Q*–*e* values

System	r_1^a	r_2	Q_2	e_2
MMA–M1	1.3315	0.00005	1.920	3.50
MMA–M2	1.1568	0.16814	1.067	1.68
MMA–M3	1.2333	0.00010	1.990	3.40
MMA–M4	1.1320	0.00006	2.250	3.50
MMA–M5	1.5880	0.00005	1.593	3.47

[a] MMA was considered as the first monomer

The data acquired from simultaneous TGA-DSC analysis (see Table 1) of the entire new series of poly(methacrylate)s provided additional information about the influence of the chemical composition upon the thermal stability and the glass transition temperatures (T_gs). Thus, a higher content of azo-moieties led to a slightly decreased thermal stability (in any considered system) accompanied by increased T_g values. The chemical linkage of chromophores onto the backbone increased the glass transition temperatures of the final copolymers, as compared to pristine PMMA (see Fig. 1). The influence of the substitution pattern was visible; the best thermal stability was recorded for MMA–M1 and MMA–M2 structures (see Fig 2), due to the single *para*-substitution on the second aromatic ring (–CN or –NO_2). The structures with –NO_2 substituents exhibited better thermal stability and lower T_g

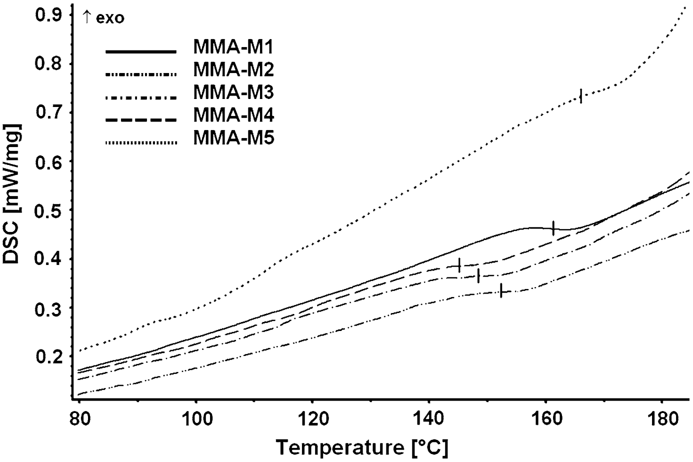


Fig. 1 DSC curves for MMA–Mx copolymers with 7:3 feed molar ratios

values than the ones with –CN substituents. Again, due to the *ortho*- substitution with a chlorine atom, the MMA–M5 systems exhibited the most unusual thermal features unparalleled by any other studied system. Consequently, the MMA–M5 (7:3) system exhibited the highest T_g and the lowest thermal stability. For each MMA–Mx system, the higher M_w is the higher is the T_{onset} (see Table 1). In the MMA–M2 series the MMA–M2 (9:1) system exhibited the highest thermal stability ($T_{onset} = 306$ °C, see curve in Fig. 2) for the highest recorded M_w. The weight loss at 700 °C was provided in Table 1 for all copolymer structures; the increase of

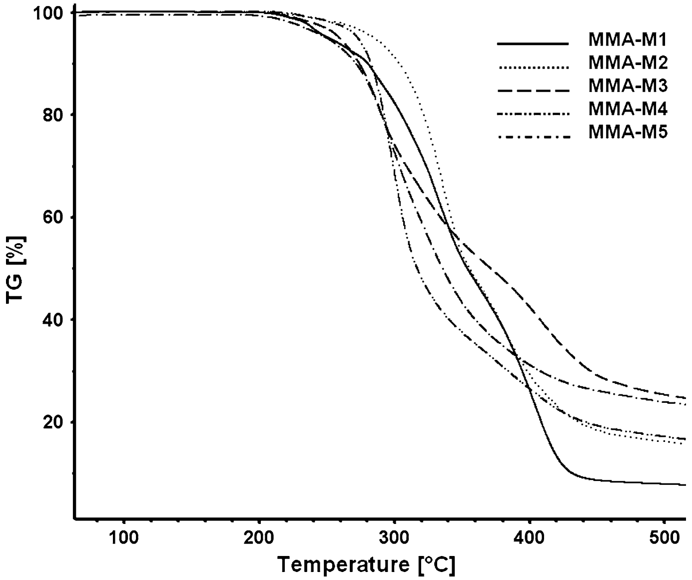


Fig. 2 TGA curves for MMA–Mx copolymers with 9:1 feed molar ratios

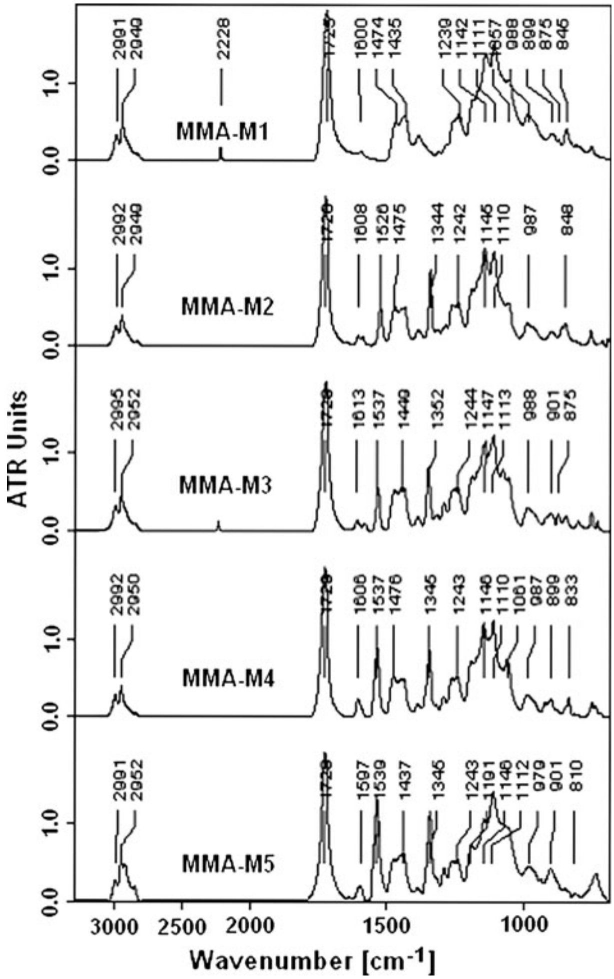


Fig. 3 FT-IR spectra for MMA–Mx copolymers for 8:2 feed molar ratio

azo-moieties along side-chains in all our systems led, as expected, to a higher percentage of residue (i.e., lower weight loss), due to aromatic rings.

The chemical structure of the copolymers was identified by FT-IR and ^{1}H-NMR spectroscopy. Representative examples for the FT-IR spectra of MMA: Mx = 8:2 and for the ^{1}H-NMR spectra of MMA: Mx = 7:3 polymers are given in Figs. 3 and 4, respectively.

The FT-IR spectra confirmed the chemical structures, which exhibited all absorption bands attributed to functional groups present in the polymers: 1730 ($\nu_{C=O}$) and 1110 ($\nu_{C\text{–}O}$); 2230 (ν_{CN}), 1435 and 1475 ($E\ \nu_{N=N}$), 1535 and 1350 (ν_{NO_2}) from azo-moieties, 2950 (ν_{CH_2}), all in cm^{-1}. The absorption bands at 3080 and 1608 cm^{-1} attributed to C=C vinyl bonds were weakening along with the

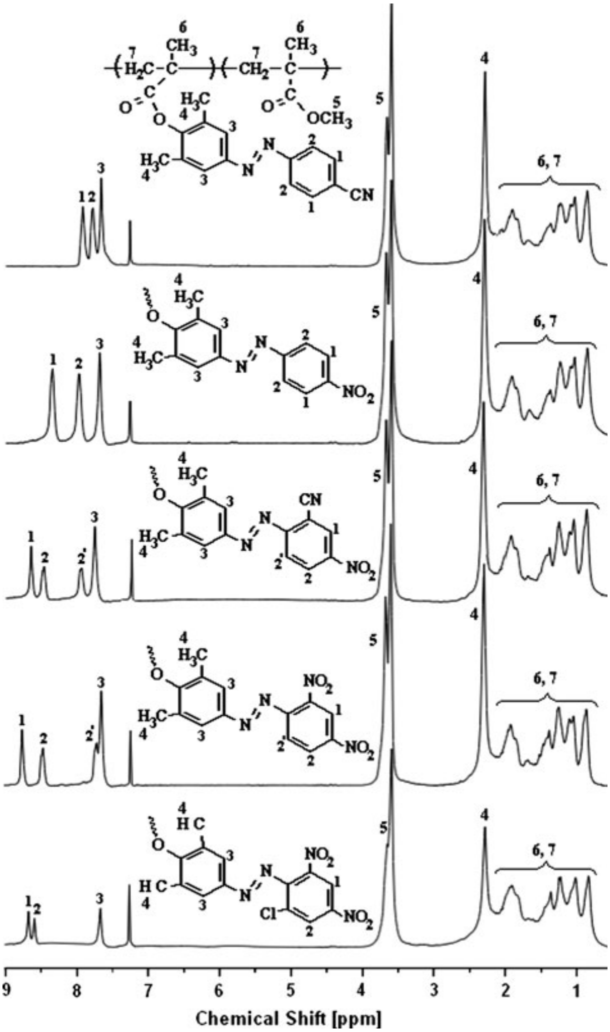


Fig. 4 ^{1}H-NMR spectra for MMA–Mx copolymers for 7:3 feed molar ratio

copolymer formation. This fact indicated that the radical polymerization proceeded via vinyl-type polymerization.

^{1}H-NMR spectra showed that the proton signals belonging to the vinyl bonds from both monomers disappeared from $5 \div 6.5$ ppm and new signals appeared at $0.5 \div 2.5$ ppm (H_7); this indicated that all the double bonds were consumed and the copolymers were obtained. Between $7.5 \div 9$ ppm, we can find the corresponding aromatic proton signals ($H_{1,2,2',3}$) from each studied azo-moiety and at 2.2 ppm the peaks belonging to the ortho, ortho′-methyl groups (H_4). In the range of $0.5 \div 2$ ppm all backbone protons overlapped ($H_{6,7}$) and at 3.7 ppm we can find the methoxy group signals alone (H_5), in all spectra.

Conclusions

This study can provide valuable information regarding each particular system, underlining some of its advantages and disadvantages when choosing a certain monomer structure for designing polymers. Therefore, we learnt that the nature and the number of the substituents could lead to different physical properties. Accordingly, we noticed that when the monomer bears only a –CN group (MMA–M1 systems), the yields and molecular weights are increased as compared with the rest of the systems. Nevertheless, if a high thermal stability is desired or required, then the best choice would be the MMA–M2 systems ($T_{\mathrm{onset}} = 306$ °C) containing one $-NO_2$ group only, followed by MMA–M1 systems ($T_{\mathrm{onset}} = 285$ °C). The same situation can be found in the MMA–M3 and MMA–M4 series; the highest thermal stability was recorded for MMA–M4 (9:1) system ($T_{\mathrm{onset}} = 281$ °C) which has an *ortho-* and *para-* substitution with $-NO_2$ groups; followed by MMA–M3 (9:1) system that has both -CN and $-NO_2$ groups ($T_{\mathrm{onset}} = 262$ °C). If a higher content of azo-moieties is desired in copolymer's side-chains, the systems possessing only nitro substituents are the best choice; the highest molar composition was found for MMA–M2 (7:3) system (MMA/M2 = 3.2, which converted to a weight composition can be written as MMA/M2 = 0.94). This fact was in good agreement with the reactivity ratio obtained for *M2* monomer ($r_2 = 0.16814$) indicating that this particular monomer exhibits improved reactivity in copolymerization towards its partner. We can not overlook the fact that the glass transition temperatures are increased as compared to the PMMA matrix alone and remained in the same range (except for MMA–M5 systems), no matter the nature of the substituents (or number) from the azo-moieties. The MMA–M5 system was the most intriguing of all since we have registered unusual molecular weights, polydispersities, and surprisingly they exhibited the highest $T_g s$; all these due its supplementary chlorine atom. From the point of view of optical properties, provided by UV–Vis spectroscopy, they remain virtually unchanged in the final polymer no matter the structure we choose; this conclusion was made based on the molar extinction coefficients determined for copolymers compared to those of the previously reported monomers [34].

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