Aromatic structure influence on the selectivity of substituted methacryloylaminophenylmethacrylates free-radical polymerization

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A new dimethacrylic monomer with biphenylbenzoate-type aromatic core was tested to the possibility to carry out its selective homopolymerization under conditions of thermoinitiated radical polymerization in DMF solution. The kinetics of thermo-induced radical homopolymerization of this monomer as well as some model compounds were studied by dilatometry. The preferring polymerization of O-methacryloyl double bond was proved by ^{1}H NMR spectroscopy.

Introduction

In our recent approaches it has been developed efficient polymers for liquid crystal (LC) photoalignment. The most promising of them were obtained with free radical polymerization of methacryloylamino-arylmethacrylates having two polymerizable methacryloyl groups of different reactivity and linear aromatic core [1-2]. It was shown that reactions of residual side-chain methacrylic groups strongly improve the alignment stability [3].

The presented study is devoted to the investigations of structure influence of a new biphenyl-containing monomer M1 on the possibility to carry out its selective homopolymerization under conditions of thermoinitiated radical polymerization in DMF solution. In addition, model monomers having only one type of polymerizable bond were synthesized and tested at the same conditions to elucidate an individual contribution of

methacrylate and methacrylamide group in polymerization rate and crosslinking at the polymerization of M1. The structures of model compounds are simplified so that compound Mod1 contains only methacrylamide ($NHCO(CH_3)C=CH_2$) polymerizable double bond as well as compound AAPhMA contains methacrylate ($OCO(CH_3)C=CH_2$) polymerizable bond.
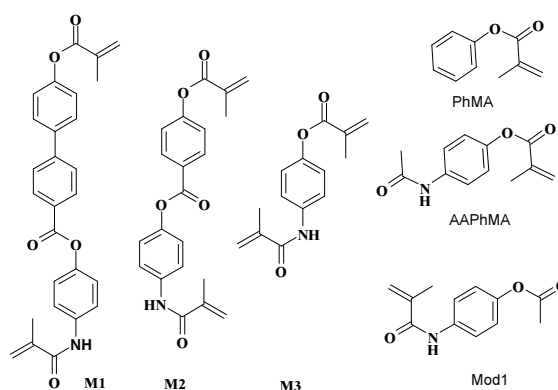

Figure 1. Chemical formulas of studied monomers.

Results and discussion

Homopolymerization of asymmetrical divinyl monomers M1-M3 can be considered as

homopolymerization copolymerization of two types of the reactive double bonds. The reactivities of substituted O-methacryloyl and NH-methacryloyl groups could be estimated through *Q* and *e* values [4] of model monomers p-acetylaminophenylmethcrylate (AAPhMA) (Q_1= 1.75, e_1= 0.31) and N-(*p*-phenyl)-methacrylamide (PhMA) (Q_2=0.85, e_2 =-0.78).

The reactivity ratios [4] were calculated based on Alfrey-Price equations: $r_1=(Q_1/Q_2)\exp[-e_1(e_1-e_2)]$; $r_2=(Q_2/Q_1)\exp[-e_2(e_2-e_1)]$. (Q,e) values of PhMA and AAPhMA are cited from [5] and [6] respectively. Quantitative analysis using Alfrey-Price equations gave estimated reactivity ratios r_1 of about r_1=1.47, r_2=0.21 and r_1/r_2=7.00 for bifunctional monomers M1-M3. These values indicate that the *O*-methacryloyl groups have higher reactivity but not significantly than do the *NH*-methacryloyl. In addition, negative and positive values of e_2 and e_1 indicate a tendency to copolymerization of O-methacryloyl and NH-methacryloyl groups. So, previous theoretical estimates indicate relatively low capacity for selective polymerization of O-methacryloyl double bond at the presence of NH-methacryloyl one in monomers M1-M3.

Theoretical conclusions were confirmed by comparizon of kinetic data obtained for bifunctional monomers M1-M3 as well as for model monofunctional monomers Mod1 and AAPhMA. The kinetics of thermo-induced radical homopolymerization of these monomers was studied by dilatometry. Thermo-initiated radical polymerizations were conducted at 80°C

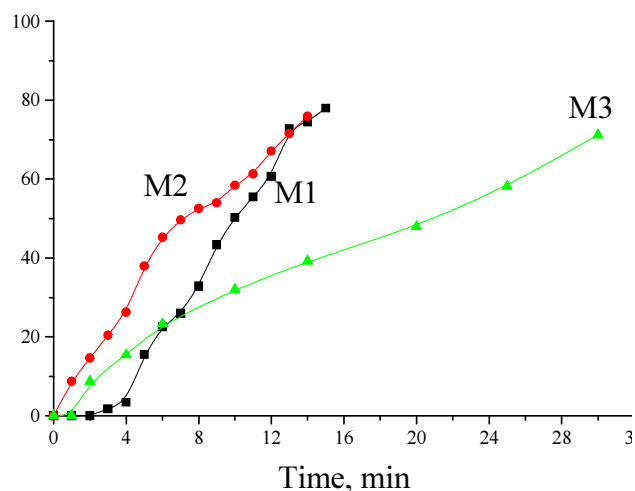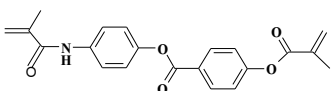using 0.172 M concentrations of monomers in DMF and 0.0023 M concentration of 1wt.% AIBN towards monomer weight.
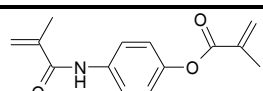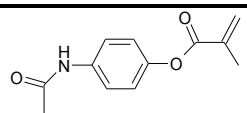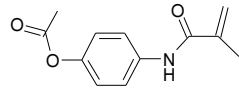

Figure 2. Conversion as a function of polymerization time for monomers M1, M2 and M3.

Calculated from experimental kinetic curves (Figure 2) parameter of total polymerization rate V_t was employed for further evaluation of efficient constant K_Σ of thermo- and photo-induced polymerization. The constant was evaluated from the equation $V_t=K_\Sigma[I]^{0.5}[M]$, where [I] - molar concentration of initiator, [M] - molar concentration of monomer [4]. The obtained values of K_Σ for thermo-induced radical polymerizations of bifunctional and model monomers are presented in Table 1.

Table 1. Efficient polymerization constant K_Σ of thermo-induced polymerization of monomers M1-M3 and model monomers.

Bifunctional monomers	K_Σ, $l^{0.5}/(mol^{0.5}\times s)$
M1	12.65×10^{-3}

M2	6.30×10^{-3}
M3	5.90×10^{-3}
Model monomers	K_{Σ}, $l^{0.5}/(mol^{0.5}\times s)$
AAPhMA	3.80×10^{-3}
Mod1	0.18×10^{-3}

Data presented in Table 1 could be summarized in the next conclusions:

- Comparing efficient constants K_{Σ} of monofunctional monomers AAPhMA and Mod1 confirms theoretical prediction of higher reactivity of O-methacryloyl (K_{Σ} (AAPhMA)=3.80×10^{-3} $l^{0.5}/(mol^{0.5}\times s)$) double bond in comparizon with NH-methacryloyl one (K_{Σ} (Mod1)=0.18×10^{-3} $l^{0.5}/(mol^{0.5}\times s)$).

- Both efficient constants K_{Σ} of thermo-induced polymerization of monomers M3 (K_{Σ}=5.90×10^{-3} $l^{0.5}/(mol^{0.5}\times s)$) and M2 ($K_{\Sigma}$=$6.30\times10^{-3}$ $l^{0.5}/(mol^{0.5}\times s)$) are close to monofunctional monomer AAPhMA (K_{Σ}=3.80×10^{-3} $l^{0.5}/(mol^{0.5}\times s)$). This may be indirect evidence of the preferring polymerization of O-methacryloyl double

bond in bifunctional monomers M2 and M3 at the initial stage of the process.

- In contrast, K_{Σ} of monomer M1 (K_{Σ}=12.60×10^{-3} $l^{0.5}/(mol^{0.5}\times s)$) is 2-3 times of magnitude higher. The observed increase in selectivity in the case of poly-M1 can be explained by the influence of steric factor associated with the presence of bulky aromatic core in bifunctional monomer M1.
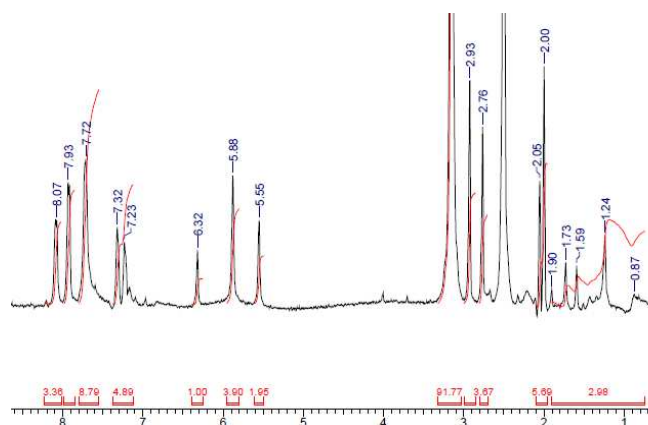

Figure 3. Fragment of ^{1}H NMR spectrum of Poly-M1 at monomer conversion 36 wt.%.

The soluble poly-M1, poly-M2 and poly-M3 polymers obtained were analyzed by ^{1}H NMR spectroscopy for quantitative determination of each type of free double bonds. The resonance intensities ratio of the CH_2= protons in NH-methacryloyl group at 5.55-5.41 ppm and CH_2= protons in O-methacryloyl group at 6.35-6.24 ppm indicates that O-methacryloyl group were polymerized with higher conversion then NH-methacryloyl finally giving polymer with two type of side alken functionalities. The molar ratio NH-methacryloyl:O-methacryloyl free side bonds in poly-M1 is around 1.00:0.52 at monomer conversion ~36 wt.% (Figure 3); in poly-M2 is around 1.00:0.88 at monomer

conversion ~36 wt.% and in poly-M3 is around 1.00:0.67 at monomer conversion ~35 wt.%. Nevertheless, in all cases selective polymerization of O-methacryloyl groups in monomers M1-M3 is limited by low (up to ~40-45 wt.% monomer conversion) yield of soluble polymer product.

Conclusions

The preferring polymerization of O-methacryloyl double bond in bifunctional monomer M1 and its analogues at the initial stage thermo-induced radical polymerization was proved. An increase in selectivity in the case of homopolymerization of bifunctional monomer M1 can be explained by the influence of steric hindrance associated with the presence of bulky biphenylbenzoate-type aromatic core.

Experimental part

All solvents of p.a. quality (Aldrich) were stored over molecular sieves of 3 or 4 Å. Other chemicals were purchased from Aldrich and used without further purification. Monomers M1, M2 and M3 were prepared in one or three steps synthetic procedures. Thin layer chromatography was performed on Merck Kieselgel plates 60-F254. ^{1}H NMR spectra were recorded with a Varian 400 NMR spectrometer with tetramethylsilane as internal standard in DMSO-d_6 as solvent.

Synthetic procedures

Bifunctional monomer M1 was synthesized as described in [7] by acylation of 1,4-aminopenole with (meth)acryloylchloride in dry tetrahydrofuran (THF).

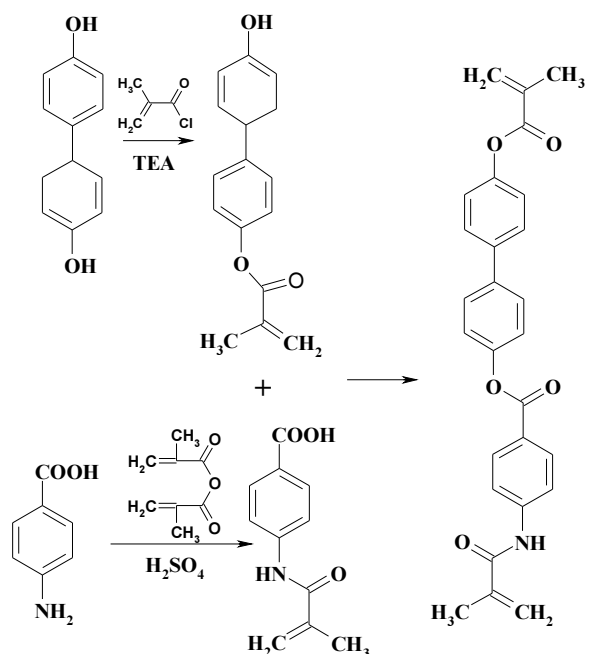Yield 72 wt.%. M.p.: 103-105°C. R_f – value (acetone:hexane:benzene= 4:5:7)= 0.93.

^{1}H NMR (400 MHz, DMSO-d_6), ppm: 9.71 (s, 1H, NH); 7.72 (d, 2H, Ar), 7.01 (d, 2H, Ar); 6.27(s, 1H, C$\underline{H}_2$=C(CH$_3$)COO); 5.81 (s, 1H, C$\underline{H}_2$=C(CH$_3$)COO); 5.80 (s, 1H, C$\underline{H}_2$=C(CH$_3$)CONH); 5.47 (s, 1H, C$\underline{H}_2$=C(CH$_3$)CONH); 2.02 (s, 3H, CH$_3$); 1.97 (s, 3H, CH$_3$).

Monomer M2 was prepared in three steps synthetic procedure: the first two stages of the synthesis of intermediate 4-(methacryloyloxy)benzoic acid and 4-methacryloylaminophenol. The third step was the condensation previously obtained compounds in THF.

Yield 29 wt.%. M.p.: 145-146°C. R_f – value (acetone:hexane:benzene= 7:5:10)= 0.39.

^{1}H NMR (400 MHz, DMSO-d_6), ppm: 9.74 (s, 1H, NH); 8.22 (d, 2H, Ar); 7.78 (d, 2H, Ar); 7.33 (d, 2H, Ar); 7.11 (d, 2H, Ar); 6.35 (s, 1H, C$\underline{H}_2$=C(CH$_3$)COO); 5.89 (s, 1H, C$\underline{H}_2$=C(CH$_3$)COO); 5.82 (s, 1H, C$\underline{H}_2$=C(CH$_3$)CONH); 5.46 (s, 1H, C$\underline{H}_2$=C(CH$_3$)CONH); 2.05 (s, 3H, CH$_3$); 1.99 (s, 3H, CH$_3$).

Monomer M3 was prepared in three steps synthetic procedure in accordance with the scheme:

Yield 80 wt.%. M.p.: 210-212°C. R_f − value (acetone:hexane:benzene= 2:1:4)= 0.85.

^{1}H NMR (400 MHz, DMSO-d_6), ppm: 2.00 (s, 3H, $CH_2 =C(CH_3)$-CONH); 2.05 (s, 3H, $CH_2=C(CH_3)$-COO); 5.54 (s,1H, $CH_2 =C(CH_3)$-CONH); 5.86 (1H, $CH_2=C(CH_3)$-COO); 5.88 (s,1H, $CH_2=C(CH_3)$-CONH-); 6.32 (s,1H, $CH_2=C(CH_3)$-COO); 7.21 (d, 2H, Ar); 7,32 (d, 2H, Ph); 7.73(m, 4H, Ar); 7.92(d, 2H, Ar); 8.08 (d, 2H, Ar); 10.05 (s,1H, NH).

Polymerization procedure

The kinetics of the monomers were studied by dilatometry under argon using DMF as a solvent. The yield of the polymers was determined by gravimetry. The solution of 0.172 mol/l of monomer M1, M2 or M3 was heated to 80 °C at the presence of 0.0023 mol/l of 2,2'-azobis(isobutyronitrile) (AIBN) as initiator.

References

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