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New polymethacrylic nonlinear optical materials containing multichromophores in the side chain

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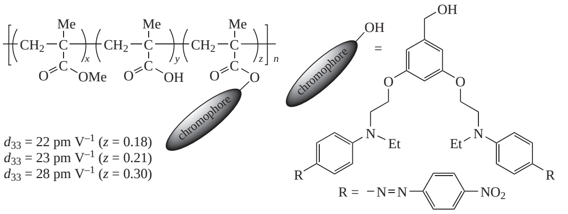
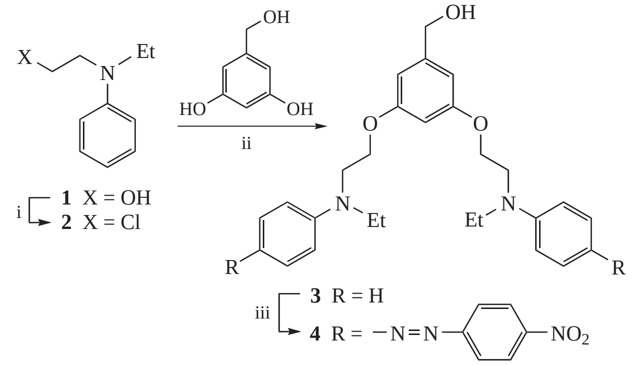
New polymer materials based on methacrylic copolymers with chromophore-containing dendritic fragments in the side chain have been obtained. The nonlinear optical coefficients of 22, 23 and 28 pm V^{-1} have been determined for polymers with 18, 21 and 30 mol% content of dendritic fragments, respectively.



Methacrylic copolymers are traditionally used to create materials with quadratic nonlinear-optical (NLO) response to the high-intensity electric field (see refs. 1–3 and references cited therein). Organic dipole chromophores responsible for the NLO effect at the molecular level are introduced into the polymer matrix either as guest molecules or by their covalent attachment to the polymer chain.[1,4] To exhibit quadratic NLO response, the material should be non-centrosymmetric, which is achieved by the orientation of dipolar chromophore groups in the applied electric field. Establishment of the optimal content of chromophores in the matrix is an important task since their excess can cause an aggregation due to detrimental dipole–dipole interaction (DDI) leading to a decrease in NLO activity. One way to reduce the probability of such a DDI is to tune polymer structure towards chromophore spatial separation. Such requirements are typical, in particular, of branched polymers[5–7] or polymers with dendritic multichromophore fragments in side chains.[8–10] Earlier, we exemplified this approach by epoxy-amine oligomers with dendritic fragments in the side chains.[11] The present work is devoted to the synthesis of linear copolymers of methyl methacrylate (MMA) and methacrylic acid (MAA) with multi-chromophore fragments in the side chain.

Synthesis of chromophore from available 2-(*N*-ethylanilino)ethanol **1** is outlined in Scheme 1. The final 3,5-bis{2-[*N*-ethyl-4-(4-nitrophenyldiazenyl)anilino]ethoxy}benzyl alcohol **4** (DF1), having an aromatic branching center and ethylene groups tethering the chromophores to this center was supposed to be an NLO-active compound responsible for the manifestation of a quadratic NLO effect at the molecular level.[12] When preparing the compound, the described[13] synthetic approaches were taken into account as a basis.



Scheme 1 *Reagents and conditions*: i, POCl$_3$, 100 °C, 1 h, 50%; ii, K$_2$CO$_3$, KI, DMF, 85 °C, 48 h, 30%; iii, [4-O$_2$NC$_6$H$_4$N$^+$≡N]BF$_4^-$, DMF.

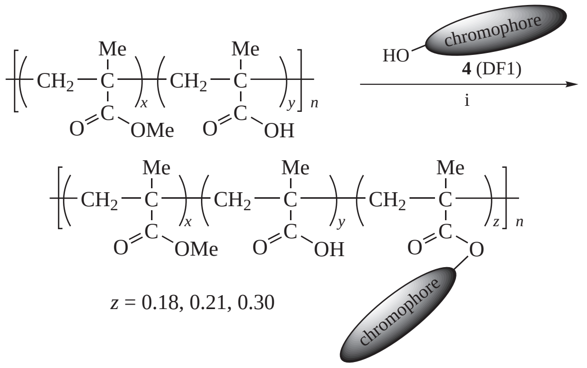
The use of reported chlorination procedure[14] made it possible to increase the yield (up to 50%) of intermediate chloro aniline **2** by a factor of about four. Synthesis of 3,5-bis[2-(*N*-ethylanilino)ethoxy]benzyl alcohol **3** was carried out in DMF at 85 °C (see Scheme 1). The product was purified by column chromatography (hexane–CH$_2$Cl$_2$–acetone, 1 : 1 : 1.5). Azo coupling of bis-aniline **3** brought about dye DF1 **4** as a dark red powder with T_m 163 °C.

Methacrylic copolymers were prepared in DMF solution by radical copolymerization at different MMA and MAA ratios at in the presence of 2% azobisisobutyronitrile (AIBN) at 70 °C for 5 h. The copolymers were obtained in good yields (Table 1), their structure was confirmed by physicochemical methods. In their IR spectra, absorption bands corresponding to the following groups were observed: 3260 cm^{-1} (OH); 2995, 2950 cm^{-1} (CH$_2$); 1732 cm^{-1} (C=O); 1239, 1149 cm^{-1} (C–O–C). The ^{1}H NMR spectra were used to calculate the composition of the copolymers.

As seen from Table 1, for all compositions the MAA content in the copolymer exceeds its content in the initial mixture. Their characteristic viscosities [η] are in general close to 0.2 dl g^{-1}, giving evidence to a weak dependence of copolymers molecular weight

Table 1 Physicochemical characteristics for MMA–MAA copolymers.

MAA content (mol%)		Yield of copolymer (%)	Viscosity, [η]/dl g^{-1}	T_g/°C (DSC)	T_d/°C (TGA)
In initial mixture	In copolymer (^{1}H NMR)				
5	8	72	0.202	–	270
10	20	76	0.218	68	296
20	29	85	0.182	78	307
30	39	74	0.207	–	311
40	46	86	0.201	93	315



Scheme 2 *Reagents and conditions*: i, DCC, DMAP, THF, 25 °C.

on their composition. The glass transition temperature (T_g) of copolymers grows with the increase in MAA content, which is apparently due to the formation of a physical network in the copolymers. The same trend is observed when comparing the thermal stability of copolymers.

The introduction of chromophores into the copolymers was carried out by the Steglich esterification reaction under mild conditions (Scheme 2). The modified copolymers appeared as red powders easily soluble in polar solvents. Their structure was confirmed by physicochemical methods. In their IR spectra, absorption bands corresponding to the groups characteristic of MMA–MAA copolymers were retained, and new absorption bands corresponding to the multi-chromophore fragments appeared: 1600, 1588, 1446 cm^{-1} (arene); 1253, 1139 cm^{-1} (C–O–C); 1386 cm^{-1} (N=N); 1513, 1336 cm^{-1} (NO_2). Their ^{1}H NMR spectra contained signals for the *ortho*- and *meta*-protons of azobenzene moieties as doublets at 6.93, 7.90, 7.95 and 8.33 ppm; signals for the *ortho*- and *para*-protons of the aromatic branching center at 6.57 and 6.38 ppm, respectively, and a broad signal at 4.5 ppm for the benzylic methylene protons tethering the dendritic fragments to the oligomer chain. Moreover, in the region of 3.9 and 4.2 ppm, the signals of the ethylene tether groups are manifested, the methyl protons resonate at 1.26 ppm. Signals for the hydroxyl group (*ca.* 11 ppm) are absent. Proton signals of the polymer chain at 3.67 ppm (MeO), 1.86–1.93 ppm (CH_2) and 1.17–1.05 ppm (Me) are regularly present.

The UV-VIS spectra of functionalized copolymers were recorded in THF solution at the polymer concentration of 2×10^{-5} mol dm^{-3} (Figure 1). The presence of a broad peak at 300 nm corresponds to electronic π–π* transitions for aromatic rings; and a more intense symmetric absorption band in the long-wavelength region with λ_{max} = 472–476 nm is due to superimposed n–π* and π–π* transitions of azobenzene chromophore groups. Some characteristics of the resulting chromophore-containing copolymers are given in Table 2. The concentration of DF1 units and the degree of functionalization were determined from ^{1}H NMR spectra.

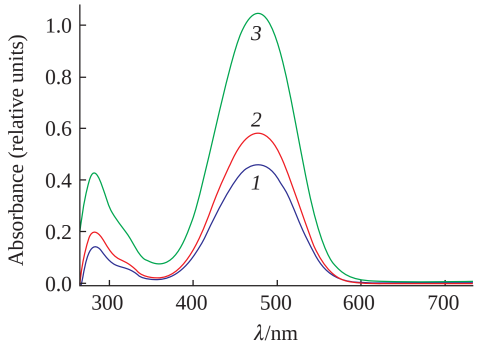


Figure 1 UV-VIS spectra of methacrylic copolymers with different DF1 content: (*1*) 18, (*2*) 21, and (*3*) 30 mol%.

Table 2 Physicochemical properties of DF1-modified copolymers.

DF1 content (mol%) (^{1}H NMR)	Functionalization degree (%)	Yield of modified copolymer (%)	T_g/°C (DSC)	$T_{10\%}$/°C (TGA)
18	90	92	96	291
21	73	88	72	276
30	77	53	95	263

Table 3 Characteristics of DF1-modified copolymer film.

DF1 content (mol%)	Film thickness/nm	T_p/°C	Φ	d_{33}/pm V^{-1}
18	290	110	0.38	22
21	310	110	0.25	23
30	297	110	0.19	28

According to the presented data, the degree of functionalization and yield of chromophore-containing copolymers decrease with raising the MAA content in the copolymer composition, which is apparently associated with steric hindrances.

With increase of the chromophore concentration, the thermal stability of the copolymers decreases, which can be explained by the lower thermal stability of the chromophore itself (T_d = 250 °C). The copolymers obtained have good film-forming properties; the thickness of the cast films measured by the AFM method is 290–310 nm.

The resulting films were transferred to the electret state in the corona discharge field using the standard procedure.[15] Order parameter (Φ) characterizing the efficiency of chromophore orientation, is determined from the UV-VIS spectra by the change in absorption intensity of the film before and after poling.[15] NLO coefficients (d_{33}) of the obtained materials, determined by the SHG technique (Nd^{3+}:YAG laser, λ = 1064 nm, pulse duration 15 ns, power density on the sample 10 kW cm^{-2}) are given in Table 3.

As can be seen from Table 3, the values of NLO coefficients increase with raising the concentration of chromophores. The data we obtained earlier for materials based on epoxy-amine oligomers with multichromophore dendritic fragments showed that sufficiently high values of NLO coefficients could be achieved by performing the poling at the temperature T_p exceeding T_g by ~30 °C.[16] Taking this into account, we can expect the d_{33} values of the obtained materials to increase upon optimizing the poling regime.

Repeated d_{33} measurements performed after four months showed a decrease in the NLO response by ~60%. To enhance the relaxation stability of the response, we propose to perform cross-linking of the copolymer chains by addition of glycidyl methacrylate to the obtained copolymers.

In summary, we have obtained novel polymer materials based on methacrylic copolymers with dendritic chromophore-containing fragments (DF1) in the side chain, which demonstrate rather high nonlinear optical coefficients. The best value of 28 pm V^{-1} was found for dendritic fragment content of 30 mol%.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2018.05.014.

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