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Nonlinear-optical properties of methacrylic (co)polymers with azo chromophores in the side chain

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The efficiency of a two-stage procedure for the synthesis of methacrylic copolymers with azo chromophores in the side chain exhibiting quadratic nonlinear optical activity was demonstrated.

The development of new nonlinear optical (NLO) polymers for applications in photonics and optoelectronics is of importance for modern materials science.[1–3] To study the quadratic NLO activity formed at the molecular level due to incorporated organic chromophores, polymer materials are transformed into an electret state with frozen-in macroscopic polarization arising as a result of chromophore groups orientation in the applied electric field.[1–3] Methacrylate copolymers with chromophores in the side chain historically were one of the first classes of studied NLO polymers.[1,2] However, they attract close attention of the researchers up to now.[4–7] Here, we report the NLO activity of methacrylate polymers and copolymers with 4-amino-4′-nitroazobenzene groups in the side chain synthesized by a two-stage procedure allowing to obtain both copolymers and homopolymers with high chromophore concentrations.

Two-stage synthesis of NLO oligomers is described in ref. 8, the essence of the approach is the following: at the first stage the aniline-containing oligomer precursor is synthesized, serving as azo component in azo functionalization performed at the second stage. Aniline-containing monomer, *N*-methylaniline hydroxypropyl methacrylate (AMA) has been obtained by the reported procedure.[9] This monomer was used in the synthesis of oligomeric precursor by radical polymerization or its copolymerization with methyl methacrylate (MMA) at equimolar ratio of monomers in DMF solution at 80 °C, azobisisobutyronitrile being used as initiator of polymerization. The second stage of the reaction was azo-coupling with *p*-nitrobenzene diazonium tetrafluoroborate being used as diazo component. As a result we obtained homopolymer 4′-[*N*-methyl-*N*-(3-methacryloyloxy-2-hydroxypropyl)]-amino-4-nitroazobenzene (PMAZ) (yield, 85.5%; M_n = 10 200) and copolymer MMA-co-MAZ (yield, 91.2%; M_n = 14 400).

The structure of the obtained polymers was confirmed by physico-chemical techniques. Azo-functionalization was controlled by UV, IR and ^{1}H NMR spectroscopy. Analysis of the ^{1}H NMR spectrum shows that, as a result of azo-functionalization in the aromatic region of the spectrum the following three wide singlets appear instead of two singlets near 7.23 and 7.76 ppm corresponding to (*p*-H + 2*o*-H) and 2*m*-H of the aniline fragment in the initial copolymer: δ 8.30 ppm, corresponding to *ortho*-protons with respect to NO_2 group; δ 6.83 ppm with respect to –N=N– group; and δ 7.91 ppm with respect to NMe group, an intensity ratio of 2 : 4 : 2.

In the IR spectrum of the functionalized (co)polymers, absorption bands were observed at 1339 and 1518 cm^{-1}, corresponding to symmetric and antisymmetric stretching vibrations of the nitro group, and at 1376 cm^{-1} attributed to azo group vibrations. According to analysis with respect to nitrogen, the molar concentration of functionalized AMA in copolymer is 45 mol%; the degree of functionalization is approximately 96% in both cases. Synthesized polymers have been obtained as red powders well-soluble in organic solvents.

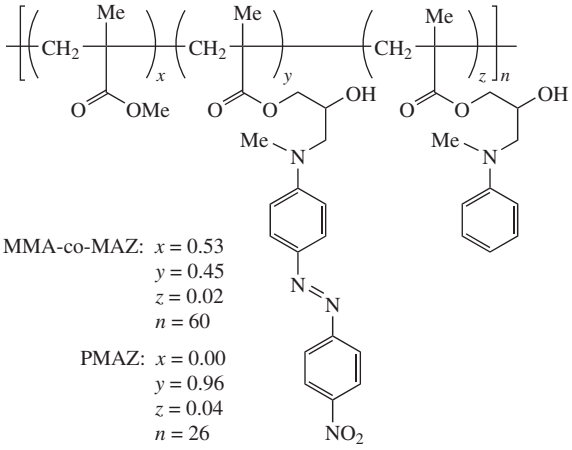

Figure 1 Structure of the synthesized methacrylic oligomers.

The azo-functionalization technique used in this work has advantages over the radical copolymerization of individual chromophores: copolymers are obtained with high degree of functionalization (~96%) and in good yield (up to 91%) without preliminary synthesis, isolation and purification of chromophore-monomer; moreover, polymer azo-coupling reaction proceeds under milder reaction conditions, not requiring tight control over medium pH and temperature.

Since the obtained polymers contain reactive hydoxy groups, on their basis the cross-linked NLO polymers have been synthesized *via* hardening by 4,4′-diphenylmethane diisocyanate (MDI).

To study the NLO activity of the obtained polymers, thin films were spin-cast from a 7% polymer solution in cyclohexanone by the procedure described elsewhere.[10] Film thickness *h* (Table 1) was determined by atomic-force microscopy in intermittent-contact mode. Poling procedure was carried out in the corona-discharge field (voltage, 6.5 kV) at a poling temperature of 110–130 °C. The quality of chromophores orientation was controlled by UV-VIS spectroscopy by a change in film absorption intensity before and

Table 1 Characteristics of methacrylic polymer films.

Oligomer/polymer	Chromophores (mol%)[a]	*h*/nm	T_g/°C	T_{pol}/°C	η	d_{33}/ pm V^{-1}
PMAZ	96	230	117	120	0.17	10.0
		180		112	0.30	20.1
PMAZ + MDI	96	150	118	120	0.18	12.5
		270		130	0.16	31.4[b]
MMA-co-MAZ	43	270	124	125	0.20	31.0
		270		125	0.23	35.2
MMA-co-MAZ + MDI	43	160	164	110	0.28	37.0
		400		130	0.23	46.5[b]

[a] According to ^{1}H NMR data. [b] Changed poling regime: electric field was applied to the film heated to 80 °C, then heating was continued up to T_{pol} = = 130 °C.

after poling. The values of order parameters of the studied samples, η, were estimated to lie in a range from 0.17 to 0.30.

Quadratic NLO characteristics of the test polymers were measured by a second harmonic generation technique;[10] the fundamental beam was provided by a pulse Nd^{3+}:YAG laser (λ = 1064 nm). Measured values of NLO coefficients, d_{33}, are presented in Table 1. The values of d_{33} for PMAZ are lower than those for MMA-co-MAZ, the reason seems to be the partial aggregation of chromophore groups due to their high content in the polymer, lowering the number of chromophores capable of orienting in the applied electric field. The d_{33} values for the cross-linked polymers are higher than those for linear ones. For methacrylate (co)polymers studied here likewise the epoxyamine oligomers studied earlier,[10] we have observed the effect of the poling regime and the film preparation procedure (in particular, preliminary drying at an elevated temperature) on the values of d_{33}, the latter being of prime importance for polymer systems containing hardening agents. Taking into account published data,[4,6] one may suggest that an increase in the NLO coefficient can be achieved by lowering the chromophore concentration in a polymer matrix; however, this suggestion requires special examination. Measurements of NLO coefficient repeated in a year demonstrated a decrease in the value of d_{33} for a linear copolymer by ~27%, while d_{33} remained almost unchanged for the cross-linked polymer. Thus, methacrylate (co)polymers with NLO chromophores in the side chain synthesized by the two-stage procedure exhibit essential quadratic NLO activity. The presence of reactive groups allowed obtaining polymer networks with both NLO characteristics and their relaxation stability being higher than those of corresponding linear copolymers.

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