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Synthesis and nonlinear optical properties of branched copolymers with covalently attached azochromophores

T.A. Vakhonina [a,*], M.Yu. Balakina [a,*], G.N. Nazmieva [a], N.V. Ivanova [a], S.V. Kurmaz [b], I.S. Kochneva [b], M.L. Bubnova [b], E.O. Perepelitsina [b], N.N. Smirnov [c], A.V. Yakimansky [c], O.G. Sinyashin [a]

[a] A.E. Arbuzov Institute of Organic and Physical Chemistry KSC RASci, ac. Arbuzov str. 8, Kazan 420088, Russian Federation
[b] Institute of Problems of Chemical Physics RASci, ac. Semenov av. 1, Chernogolovka, Moscow Region 142432, Russian Federation
[c] Institute of Macromolecular Compounds RASci, Bolshoi pr. 31, 199004 Saint-Petersburg, Russian Federation

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ABSTRACT

Soluble branched chromophore-containing nonlinear optical (NLO) methacrylate copolymers were synthesized by two-stage procedure. At the first stage aniline-containing precursors were synthesized by radical copolymerization of MMA with N-methyl,N-phenylamino-2-hydroxypropyl methacrylate (AMA) in various ratios (90:10; 80:20; 70:30) with ethylene glycol dimethacrylate, EGDMA, being used as branching agent and 1-decanethiol, DT, as a chain-transfer agent. At the second stage these precursors were functionalized by 4-nitrobenzene-diazonium tetrafluoroborate giving the azofunctionalized methacrylate units, MAZ; and copolymers with NLO groups in the side chains were obtained. The synthesized copolymers were studied and some physical–chemical characteristics were determined. On the base of the synthesized copolymers thin films were spin-cast, their thickness being measured by AFM technique. The polymer films were corona-poled and the NLO characteristics were determined by second harmonic generation technique. The values of d_{33} are shown to depend noticeably on the chromophores concentration in the polymer; for various ratios of MMA:MAZ units (90:10; 80:20; 70:30) they are equal to 77 pm/V, 45 pm/V and 28 pm/V, respectively. The values of NLO coefficients of branched chromophore-containing polymers are essentially higher than those of linear analogues obtained earlier in spite of an essentially lower concentration of chromophore groups.

1. Introduction

Nonlinear optical (NLO) polymer materials with organic chromophores introduced into the polymer matrix either as guest molecules or as fragments covalently attached to the bearing chain are designed for application in photonics and optoelectronics [1–5]. Optimal value of NLO response and its temporal stability represent key characteristics to be provided at the development of such materials [1,6]. To exhibit quadratic NLO activity polymer materials should have non-centrosymmetric arrangement of dipolar chromophores, which is realized in the applied electric field [1,5]. The efficiency of the poling procedure is limited by the undesirable dipole–dipole interaction of chromophores resulting in their partial aggregation [7]. During the present decade, several new approaches are developed to avoid this undesirable effect and provide optimal macroscopic order of the chromophores in a polymer matrix, in

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[*] Corresponding authors. Tel.: +7 (843)2727343.
E-mail addresses: TanyaVakhonina@yandex.ru (T.A. Vakhonina), mbalakina@yandex.ru (M.Yu. Balakina).

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particular, those based on the use of dendronized polymers [5,8–14] and on the hyperbranched polymers containing NLO chromophores as peripheral groups [15–18].

The 3D-structure of such materials provides spatial separation of chromophores, thus restricting their undesirable interaction. Besides, a loose topological structure of hyperbranched polymers promotes an efficient poling of chromophore groups, thus producing enhanced NLO activity [15]. Hyperbranched polymers are easily accessible synthetically in comparison to dendritic polymers [17], and, moreover, they possess a number of attractive properties, such as good solubility in organic solvents, low viscosity, morphological stability and multifunctionality of their end groups; generally, the values of NLO characteristics are higher than those of their linear analogues [15–20]. A special approach to improve the macroscopic NLO activity is the introduction of additional isolating groups into the branched polymers [17–19].

The temporal stability of the NLO activity is achieved by a cross-linking of polymer chains, as well as by the formation of physical network due to intermolecular interactions. The cross-linked hyperbranched methacrylate copolymer with FTC-type chromophore groups are shown to be characterized by high glass transition temperature and demonstrate high electro-optic activity [20].

PMMA-based polymers provide good polymer matrix properties, such as a high optical transparency, low light propagation losses. Furthermore, they show a rather good processability upon the fabrication of devices. That is why, methacrylate units are often used to produce hyperbranched NLO polymers.

Here, we discuss the synthesis of branched NLO copolymers on the basis of methacrylate monomers with chromophore groups, which are obtained via a two-step procedure. In the first stage, an aniline-containing precursor was synthesized, which was then functionalized in the second stage, giving rise to copolymers with side-chain chromophore groups. On the basis of the synthesized polymers, thin films were spin-cast, corona-poled, and NLO characteristics of the poled films were measured by the second harmonic generation (SHG) technique.

2. Materials and methods

2.1. Materials

Monomers: methylmethacrylate, MMA (Alfa Aesar, 99%), ethylene glycol dimethacrylate, EGDMA, (Aldrich, 98%) were used without preliminary purification. 1-decanethiol, DT, (Alfa Aesar, 96%) was used as a chain-transfer agent. Solvents – toluene, hexane, tetrahydrofurane (THF) and cyclohexanone – were purified by standard techniques. The initiator – azobisisobutyronitrile (AIBN) – was recrystallized from ethanol. N-methyl,N-phenylamino-2-hydroxypropyl methacrylate (AMA) is obtained by the method described in [21]. Synthesis of 4-nitrobenzenediazonium tetrafluoroborate is carried out by the technique described in [22].

2.2. Synthesis of branched copolymers

2.2.1. Synthesis of branched aniline-containing copolymers

Branched aniline-containing copolymers were synthesized by means of radical copolymerization of MMA with AMA and branching agent EGDMA in toluene in the presence of DT. Molar ratios of reagents [MMA]:[AMA]:[EGDMA]:[DT] were 90:10:12:12, 80:20:12:12, 70:30:12:12, 60:40:12:12, aniline-containing copolymers **PI**–**PIV** were obtained according to those ratios. Copolymerization was carried out in a three-necked flask equipped by a reflux condenser and a thermometer in argon flow for 5.5 h in a thermostat at 80°. The content of the reaction mixture in toluene was 20 wt%; the initiator AIBN concentration was 2×10^{-2} mol/l. After the expiry of the mentioned period, the polymers were purified by the threefold precipitation from ethanol solution to hexane, filtered and dried on air till constant weight. According to the gravimetrical data, the copolymer yield is 90–95%.

2.2.2. Azofunctionalization of aniline-containing copolymers

The azofunctionalization of copolymers **PI**–**PIII** was performed in THF solution under stirring with a magnetic stirrer for 6 h at room temperature. Copolymers were purified by the threefold precipitating from THF solution to hexane and dried in vacuum at 20° till constant weight. Copolymers **FI**–**FIII** were obtained with high yields.

Example: 0.5 g of copolymer **PII** was dissolved in 15 ml THF; 0.194 g of 4-nitrobenzenediazonium tetrafluoroborate was gradually added to the solution in little portions under intensive stirring and then 0.067 g sodium acetate (one half of the calculated amount) was added. In 30 min, the other half of sodium acetate was added to the reaction mixture. The resulting mixture was stirred for 6 h. Then, non-dissolved salts were filtered off and the filtrate was precipitated to hexane. The copolymer was further purified according to the above described procedure. The yield of the final azofunctionalized copolymer was 0.4947 g (86.7%).

2.3. Methods

Molecular weights of branched aniline-containing copolymers and their functionalized derivatives were measured by gel permeation chromatography (GPC) on a Waters GPCV 2000 chromatograph with a refractometric detector and a light scattering detector WYATT DAWN HELEOS II ($\lambda = 658$ nm), THF being used as the eluent. The measurement temperature was 35°, elution rate was 1 ml/min. Absolute molecular weights of the copolymers were estimated, processing the data of a light-scattering detector by means of Astra software (version 5.3.2.20). The refraction index increment $dn/dc = 0.126$.

Glass transition temperatures of branched copolymers and their functionalized derivatives were measured on a Mettler Toledo DSC-30 differential scanning calorimeter with the heating/cooling rate 5°/min at the second or third heating/cooling cycle in the range from 0° to 150°.

The thermal stability of branched copolymers and their functionalized derivatives was studied by their thermogravimetrical analysis on a STA 409C LUXX NETZSCH synchronous thermal analyzer (Germany, 2006).