



SYNTHESIS OF A MACROMOLECULAR RAFT AGENT BASED ON AN AROMATIC POLYAMIDE

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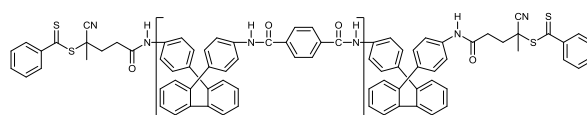
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Abstract

An aromatic polyamide with terminal amino groups was synthesized by the polycondensation of terephthalic acid dichloride with excess 9,9-bis(*p*-aminophenyl)fluorene. Its modification yielded a macromolecular bifunctional reversible addition-fragmentation chain-transfer (RAFT) agent capable of participating in the controlled polymerization for the formation of symmetrical B–A–B block copolymers.

Key words: RAFT polymerization, block copolymers, polyamide.



Introduction

RAFT copolymerization is often used to synthesize block copolymers. Therewith, the choice of the polymer chain nature is limited by the fact that all comonomers must contain a vinyl, methacrylate or other group able to take part in the radical polymerization. Recently, we have obtained ion-conducting methacrylate block copolymers, in which one of the blocks provides ionic conductivity, while the second one provides mechanical strength [1]. The microphase separation caused by the incompatibility of the blocks does not allow for averaging the properties of the blocks, alleviating the advantages of each block [2, 3].

Poly(phenylethyl methacrylate) chosen as a rigid block is significantly inferior in the deformation and strength characteristics to the polymers obtained by polycondensation, for example, aromatic polyamides [4]. Polyamides form strong elastic films, have good adhesion to various substrates, and exhibit high thermal stability and heat resistance [5, 6]. The goal of this work was to synthesize a new chain-transfer agent (**macro-RAFT**) by modifying an aromatic polyamide with terminal amino groups and to study the possibility of its application for the controlled polymerization of methacrylates. This approach will presumably afford hybrid polyamide–polymethacrylate B–A–B block copolymers with a given length of the B-blocks and high film strength, while maintaining ion-conducting properties.

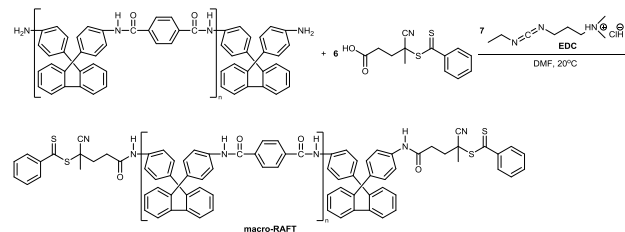
Results and discussion

The target polyamide was obtained by the low-temperature polycondensation of terephthalic acid dichloride with 9,9-bis(*p*-aminophenyl)fluorene. To ensure the presence of amino groups at the ends of the polymer chains, the diamine was taken in 1 mol % excess. The polycondensation was carried out in a

biodegradable solvent, namely, *N*-butyl-2-pyrrolidone, which is more ecologically friendly and less toxic than traditional *N*-methyl-2-pyrrolidone or *N,N*-dimethylacetamide [7].

Based on the ratio of the signals in the ¹H NMR spectrum of the resulting polyamide, corresponding to the amide groups and *ortho*- or *meta*-positions of the benzene rings in the terminal aniline units, the average degree of polymerization $n = 69$ and molar mass $M_n(\text{NMR}) = 33.4$ kDa were calculated.

Macro-RAFT was obtained by reacting the terminal amino groups of the polyamide with 4-cyanopentanoic acid dithiobenzoate, which has proven itself as an effective RAFT agent for the polymerization of methacrylates (Scheme 1). The reaction proceeded under mild conditions in the presence of 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) used for the activation of the carboxyl group.



Scheme 1. Synthesis of **macro-RAFT**.

The synthesis of a block copolymer was probed by the controlled copolymerization of lithium 1-[3-(methacryloyloxy)propylsulfon]-(trifluoromethanesulfonyl)-imide and poly(ethylene glycol) methacrylate-500 under the action of **macro-RAFT**. These monomers form an ion-conducting block, allowing the block copolymer to be used as a solid electrolyte [1]. The GPC analysis showed that, during the copolymerization, the curve peak of the resulting block copolymer shifts relative to the curve of the polyamide towards a higher molar masses (Fig. 1). At the same time, all the curves

are monomodal with a narrow molecular weight distribution, which indirectly confirms that the polymerization proceeded according to the RAFT mechanism.

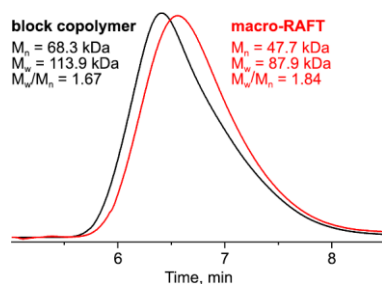


Figure 1. GPC curves of the **macro-RAFT**-based polyamide and B–A–B block copolymer.

Experimental section

Syntheses

Polycondensation. 9,9-*bis*(*p*-Aminophenyl)fluorene (3.4845 g, 10.0 mmol) was dissolved in *N*-butyl-2-pyrrolidone (20 mL). The resulting solution was cooled to -20°C . Then terephthalic acid dichloride (2.01 g, 9.9 mmol) was added. The reaction mixture was stirred at -20°C for 1 h, then 9,9-*bis*(*p*-aminophenyl)fluorene (0.035 g, 0.01 mmol) was added, and the resulting mixture was heated to room temperature and stirred for 1 h. The mixture obtained was diluted with *N*-butyl-2-pyrrolidone (40 mL) and poured into distilled water. The product (white porous fibers) was collected by filtration, washed with water, purified in the Soxhlet apparatus extracting the impurities with methanol for 16 h, and dried in a vacuum chamber at 70°C for 48 h and then at 180°C for 8 h. Yield: 4.358 g (91%). Intrinsic viscosity in *N*-methyl-2-pyrrolidone: $\eta = 0.7\text{ dL/g}$ (25°C). ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{SO}$): δ 10.4 (s, 138H, $-\text{CO}-\text{NH}-$), 7.05–8.06 (1458H, C–H Ar), 6.78–6.81 (d, 4H, *m*- $\text{C}_6\text{H}_4-\text{NH}_2$), 6.43–6.46 (d, 4H, *o*- $\text{C}_6\text{H}_4-\text{NH}_2$) ppm. $M_n(\text{NMR}) = 33.4\text{ kDa}$. GPC: $M_n = 47.7\text{ kDa}$, $M_w = 87.9\text{ kDa}$, $M_w/M_n = 1.84$ (50°C , eluent: 0.1 M solution of $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ in DMF, PMMA standards).

Synthesis of the macro-RAFT chain-transfer agent. 4-Cyanopentanoic acid dithiobenzoate (0.191 g, 0.68 mmol) was mixed with 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide hydrochloride (EDC) (0.153 g, 0.80 mmol) in DMF (20 mL). The resulting mixture was added dropwise to a solution of the polyamide (3.802 g, 0.11 mmol) in DMF (100 mL). The reaction mixture was stirred at room temperature for 3 h and poured into a mixture of acetone (300 mL) and dichloromethane (300 mL). The product was purified by the extraction with acetone in the Soxhlet apparatus for 8 h and dried in a vacuum chamber at room temperature for 48 h. Yield: 2.793 g (77%). ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{SO}$): δ 10.4 (s, 138H, $-\text{CO}-\text{NH}-$), 7.05–8.06 (1463H, C–H Ar) ppm. GPC: $M_n = 47.7\text{ kDa}$, $M_w = 87.9\text{ kDa}$, $M_w/M_n = 1.84$.

RAFT polymerization. Poly(ethylene glycol) methacrylate-500 (0.146 g, 292.8 μmol), lithium 1-[3-(methacryloyloxy)propylsulfonyl]-(trifluoromethanesulfonyl)-imide (0.020 g, 58.5 μmol), **macro-RAFT** (0.0668 g, 1.97 μmol), and azobisisobutyronitrile (0.13 mg, 0.78 μmol) were dissolved in DMF (2.5 mL). The resulting mixture was degassed

by freeze-thaw technique repeated three times and then sealed in a tube. The polymerization was carried out at 60°C for 15 h. The monomer conversion determined by NMR spectroscopy was 84%, which corresponds to $M_n(\text{NMR}) = 52.5\text{ kDa}$.

GPC studies

The molecular weight characteristics of the polymers were determined by GPC in 0.1 M solution of $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ in DMF at 50°C and a flow rate of 1.0 mL/min on a Shimadzu LC-20AD liquid chromatograph equipped with a RID-20A refractometer, Agilent PLgel 5 μm MIXED-D column (7.5 \times 300 mm), and Agilent PLgel 5 μm precolumn (7.5 \times 50 mm) using EasiVial PM:PL 2020-0201 PMMA standards (Agilent).

Conclusions

The method for obtaining the new macromolecular RAFT agent based on the polyamide was developed. The possibility of the RAFT polymerization of methacrylates, resulting in the hybrid polyamide–polymethacrylate B–A–B block copolymer, was demonstrated. This method can potentially be used to form new block copolymers with a polyamide, polyimide or polyurea central block and terminal blocks from a wide range of comonomers able to take part in the RAFT polymerization.

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