Unusual case of network polymer formation in anionic polymerization of monofunctional vinyl monomer

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Summary

Monofunctional monomers such as hydroxyalkyl (meth)acrylates can form crosslinked polymer in anionic polymerization. This unusual phenomenon relates to a plural reactivity of such type of monomers and their ability to be polymerized by the Michael addition mechanism with the formation of isomerized heterochain fragments of backbone as well as by anionic polymerization with the formation of carbon chain fragments of the main chain. This combination of reaction mechanisms results in the formation of highly branched polymer. Besides these reactions, simultaneous anionic polymerization of hydroxyalkyl (meth)acrylates, an intensive interchain exchange reaction leading to redistribution of the end functional groups and formation of polyester-ether di(meth)acrylate macromolecules result in crosslinking of the generated polymer.

Introduction

Generally, anionic polymerization of vinyl monomers bearing labile hydrogen atom yields macromolecules with backbone isomerized through Michael addition reaction [1-4]. An alkoxide anion formed in interaction of any anionic initiator with hydroxy group of monomer such as hydroxyalkyl (meth)acrylates by addition to a double bond [5-7] results in tautomeric transformations of initially generated carbanion into a much more stable enolate anion due to its conjugation with a strong electron-acceptor carbonyl group. The existence of hydrogen atom linked to a heteroatom ensures inter- and/or intramolecular reactions of proton transfer to the initially formed carbanion in each elementary event of chain propagation. As a result, isomerization of the backbone takes place and, eventually, hetero chain (polyester type) polymers arise (Scheme 1).

The presence of hydroxy group in the monomer molecule plays a key role in the formation of heterochain polymer in anionic polymerization of the vinyl monomer because of a high rate of proton transfer reaction [4-10]. As expected, in the absence of hydroxy group, anionic polymerization of acrylic monomers with protected hydroxy groups leads to the formation of carbon chain polymers. Recently, Nagasaki

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et al. [11] reported that potassium ethoxide can initiate the anionic polymerization of 2-(tetr-butyl(dimethyl)siloxy)ethyl methacrylate and 2-(diethylamino)ethyl methacrylate in THF [12]. Armes et al [13, 14] have performed anionic polymerization initiated by alcoholates of some other tertiary amine methacrylate monomers. Chinese chemists [15] reported this year on successful copolymerization of the above mentioned acrylic monomers under analogous conditions with the formation of highly branched copolymers. Recently, we described the formation of highly branched polymers in anionic polymerization of hydroxyalkyl (meth)acrylates [16, 17]. The present paper is an extension of this approach describing the mechanism of crosslinked polymer formation in anionic polymerization of 2-hydroxyethyl methacrylate (HEMA).

Scheme 1. Michael addition polymerization of 2-hydroxyethyl acrylate (HEA). Hereinafter, for the sake of simplicity, active species are denoted as free anions.

**Experimental**

**Materials**

Purification of monomers: HEA and HEMA, and their physicochemical characteristics were previously described in [4]. Metallic sodium and potassium and lithium tert-butyllate were used as anionic initiators. To prepare the alcoholate, lithium was dissolved in boiling anhydrous alcohol under dry argon. After the alcohol was distilled off, solid alcoholate was isolated in a quantitative yield.

**Instruments**

The reaction kinetics was studied by isothermal calorimetry using a DAK-1-1 thermal analyzer. Oligomers were studied by exclusion and liquid chromatography on a Waters liquid chromatograph equipped with refractometric and UV detectors. In gel-permeation chromatographic (GPC) measurements, a set of two Separon C18 (250×4 mm) columns was used, which provided a linear calibration in the range of molecular weights from 200 to 5×10^4. GPC measurements were made at a column temperature of 25°C with the use of optically pure THF; the elution rate was 0.3 ml/min. The molecular weights of polymers were calculated from GPC data using calibration plots described in [4]. In liquid chromatographic analysis under critical conditions, a column (150×4 mm) packed with a Silasorb 600 sorbent was used. The column temperature was 60°C, and