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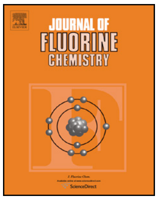

Synthesis and characterization of a novel fluorinated polyether glycol with fluorinated side chains via “living/controlled” cationic polymerization

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ABSTRACT

A novel fluorinated polyether glycol with fluorinated side chains is synthesized via “living/controlled” cationic ring-opening polymerization of tetrahydrofuran and fluorine-containing epoxy compounds (FO). The effects of polymerization conditions on monomer conversion, number-average molecular weight (M_n), molecular weight distribution (M_w/M_n) are measured. Our investigations have shown that the use of a mixed solvent (dichloromethane/1,4-dioxane) can prevent intra- and intermolecular transfer reactions, due to more nucleophilic oxygen atom in 1,4-dioxane. Using $BF_3{\cdot}CH_3OH/CH_2OHCH_2OH$ as initiation system, polymers with predictable number-average molecular weight, narrow molecular weight distribution ($1.03 < M_w/M_n < 1.08$) were produced. On the basis of the reactivity ratio of FO/THF and monomer conversion, a mechanism of living/controlled polymerization has been proposed.

1. Introduction

It is well-known that polyurethane exhibits excellent mechanical properties, thermal stability and microphase separation. Fluorinated polyurethanes, namely with fluorocarbon chains in the polyurethane, not only maintain these excellent properties, but also have very low surface energies [1,2], biocompatibility and biostability [3–7], low water absorptivity, lubricity, and oxidative stability [8]. Therefore, they are widely used as biomedical materials, anticorrosion coatings, aerospace materials, etc.

Recently, extensive works have been done on the synthesis and characterization of fluorinated polyurethanes. Fluorinated chains have been incorporated into polyurethanes via fluoro-containing diisocyanates [9], soft segments [10,11], hard segments [12–14], or chain extenders [15–19]. Because of the higher cost and fewer varieties of fluorinated dissocyanates, the synthetic route of fluorinated polyurethanes with fluorinated dissocyanates was not often used. Owing to the lower molecular weight and less fluorine content, the improvement of properties of fluorinated polyurethanes synthesized by fluorinated chain extenders was not significant. Currently, fluorinated polyurethanes are mostly synthesized using fluorinated polyether glycols as a soft segment. However, the surface properties of fluorinated polyurethane with fluorinated side chains are better than those with fluorinated groups in the main chains. This is because the fluorocarbon side chains in the polyurethane soft segments have less influence on the mechanical properties and cohesiveness of polyurethanes. Also, because of the higher mobility and flexibility of fluorinated side chains in the soft segments, fluorine groups are much easier to migrate to the surface and be enriched during molding. Therefore, the fluorinated polyurethane with lower fluorine content possesses excellent performance.

However, fluorinated polyether glycol with fluorine in the side chain is one of the most important components for further synthesis of fluorinated polyurethanes with fluorinated pendent groups. Ge et al. [20,21] successfully synthesized fluorinated polyether glycol by radical grafting of hexafluoropropylene (HFP) onto polytetramethylene glycol (PTMG) in a high-pressure reactor. Fluorinated polyurethanes with fluorine-containing pendent

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Table 1
Parameter of reactivity ratio.

Entry	x^a	y^b	G	F	ζ	H
1	3.00	3.00	2.00	3.00	0.47	0.61
2	2.00	2.00	1.00	2.00	0.78	0.38
3	1.50	1.50	0.50	1.50	0.72	0.24
4	1.00	1.00	0.00	1.00	0.63	0.00
5	0.67	0.90	−0.07	0.50	0.47	−0.07
6	0.50	0.67	−0.24	0.37	0.40	−0.26
7	0.40	0.67	−0.20	0.24	0.29	−0.24
8	0.30	0.50	−0.30	0.18	0.24	−0.40
9	0.25	0.50	−0.25	0.13	0.18	−0.34
10	0.20	0.37	−0.34	0.11	0.16	−0.50

[a] Molar ratio of monomer feed.
[b] Molar ratio in copolymer composition.

groups were then successfully synthesized. XPS and contact angle data suggested that the surface of the fluorinated polyurethanes was significantly enriched with fluorine groups.

In this work, we successfully synthesized a novel fluorinated polyether glycol (FPO) with fluorinated side chains via "living/controlled" cationic ring-opening polymerization. The advantage of the method is that the cationic active center is stable during the course of the polymerization, suspending backbiting, reversible transfer and intermolecular transfer reactions, and also, the structure and molecular weight of FPO can be precisely controlled [22–29]. Here we report a "living/controlled" cationic ring-opening polymerization leading to FPO with a controlled number-average molecular weight and narrow molecular weight distribution. The effects of polymerization conditions on monomer conversion, number-average molecular weight (M_n), molecular weight distribution (M_w/M_n) were investigated. The possible polymerization mechanism for the synthesis of FPO via "living/controlled" cationic polymerization was proposed.

2. Results and discussion

2.1. Copolymerization of fluorine-containing epoxy compounds (FO) and tetrahydrofuran (THF)

Copolymers FO–THF were prepared using different ratios of the corresponding monomers. The monomer reactivity ratio, the content of the reaction mixture and copolymer were calculated according to Kelen–Tudos method [30] (Eq. (1)). The Kelen–Tudos parameters for FO and THF are listed in Table 1.

$$\eta = \left(\mathrm{rFO} + \frac{\mathrm{rTHE}}{a}\right)\zeta - \frac{\mathrm{rTHE}}{a} \qquad (1)$$

$$\eta = \frac{G}{a+F} \qquad \zeta = \frac{F}{a+F}$$

where $G = x(y-1)/y$, $F = x^2/y$, $x = M_{\mathrm{FO}}/M_{\mathrm{THF}}$ (mol/mol), $y = \mathrm{d}M_{\mathrm{FO}}/\mathrm{d}M_{\mathrm{THF}}$ (mol/mol), and $a = x_{\mathrm{min}}x_{\mathrm{man}}/(y_{\mathrm{min}}y_{\mathrm{man}})^{0.5}$.

Fig. 1 shows a plot of ζ versus η. The monomer reactivity ratio can be determined by the slope and intercept of the straight line, $r_{\mathrm{FO}} = 0.7$ and $r_{\mathrm{THF}} = 0.4$. It can be found r_{THF} is smaller than r_{FO}, indicating that THF is less reactive than FO in the present polymerization reaction. Therefore, the FO concentration is one of the most important parameters in controlling the degree of polymerization due to the high reactivity of FO with its high reactivity ratio compared to THF. In order to effectively control the concentration of monomer, FO was added dropwise into the reaction mixture containing THF in the polymerization process. Fig. 2 shows a plot of Ln([THF]$_0$/[THF]$_t$) versus time for cationic ring-opening polymerization of FO–THF. It can be seen that Ln([THF]$_0$/[THF]$_t$) increases almost linearly with the reaction time. The good linear relationship indicates that no reversible transfer and intermolecular transfer reactions during the course of the polymerization.

Plots of number-average molecular weight (M_n) versus THF monomer conversion are shown in Fig. 3. It is clearly observed that molecular weights of the polymers increase significantly with the monomer conversions. The good linear relationship indicates that there might be polymer chains keeping active during the polymerization. Moreover, the change of molecular weights is leveling off at the latter stage of the polymerization. That is because the polymer chain propagation in the polymerization gets weak when content of active sites is low, especially at the later stage of polymerization with the decrease of the monomer concentration [31]. Owing to higher reactivity of FO with its high reactivity ratio, FO monomer acts as an active center of the chain propagation reaction, leading to the increase of the polymerization rate. When fed FO dropwise into the reaction system, the concentration of the active center could be controlled. Moreover, production and consumption of the active center are in equilibrium. These processes can decrease the rate of cationic polymerization and reflect the nature of controlled/living cationic polymerization.

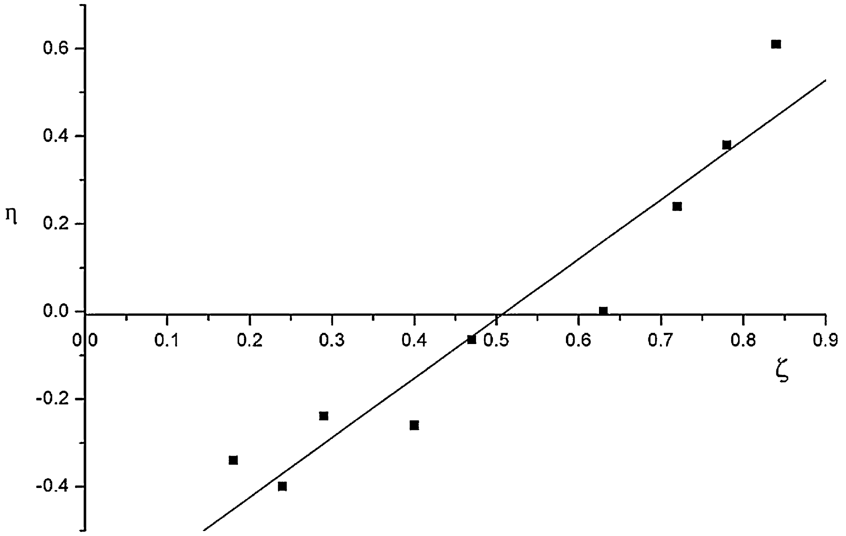

Fig. 1. Plots of ζ versus η.