

1,4-Butanediyl dimethacrylate, a photoreactive diluent, synthesized via an unusual transesterification involving glycidyl methacrylate

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Abstract

The reaction between glycidyl methacrylate and 1,4-butanediol in the presence of triethylamine was investigated. The structural analysis of the main products showed that the reaction proceeds by transesterification with release of glycidol. Transesterification occurs in two stages with, firstly, formation of the intermediate 4-hydroxybutyl methacrylate, which is thereafter transformed into 1,4-butanediyl dimethacrylate (BDMA). Whatever the conditions used, the reaction progresses similarly and at the end, an equilibrium in product composition is noticed. Under optimized conditions, it is possible to obtain yields in BDMA higher than 80%.

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1. Introduction

Current coatings use multifunctional (meth)acrylate oligomers as reagents. Because of their high molecular weight, these oligomers possess a relatively high viscosity. This later can be lowered efficiently by adding monomers as reactive diluents [1]. On the other hand, the presence of these diluents in the formulation can improve coating properties [2]. Moreover, it was reported that the photopolymerization proceeds faster by increasing the total content of the polymerizable double bond [3]. Therefore, with the intention to synthesize a difunctional methacrylate-terminated monomer to be used as a photoreactive diluent, we have studied the reaction of glycidyl methacrylate (GMA) oxirane with 1,4-butanediol (BDO). In this paper, we report on the

characterization of the reaction mechanism and the optimization of the synthesis.

2. Experimental

GMA (GC purity: 96%) was washed with NaOH 5%, then with H₂O, dried over CaCO₃, distilled over CaCl₂ under vacuum, and finally, stored in cold. BDO (99+%), solvents (THF, dioxane, and acetonitrile), and catalysts were used as obtained. Acetone was purified according to classical method [13].

¹H and ¹³C-NMR spectra were recorded on a BRUKER AC 400 MHz (respectively at 200 and 100 MHz) in CDCl₃ or CD₃OD.

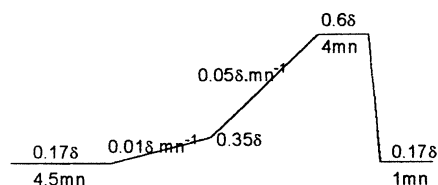
Analytical HPLC analyses were performed on a WATERS modular chromatograph equipped with two detectors (a WATERS 990 UV-vis spectrometer and a WATERS 410 differential refractometer), two Model 510 pumps and a Model U6 K injector. A Merck LiChrospher® 100 RP-18 column was used in analytical mode with MeOH/H₂O = 65/35 as eluent (flow: 1 ml/min).

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The preparative HPLC fragmentations were performed on a WATERS Delta Prep 4000 modular chromatograph equipped with two detectors (a WATERS 490E UV-vis spectrometer and WATERS 401 differential refractometer), a fraction collector. The fractionations were carried out on a WATERS Prep Nova-Pak® HR C18 column (40 × 100 mm) by using the following conditions: flow: 20 ml/min, detection by UV absorption at $\lambda = 220$ nm, eluent: MeOH/H₂O = 33/67.

Supercritical fluid chromatography (SFC) measurements were performed on an ERBA SCIENCE modular chromatograph using a SFC 300 TANDEM pumping system, a SFC 3000 chromatograph fitted with a thermostated semi-automatic “split” mode injector, an oven with a temperature programming system, a DB5 capillary column (stationary phase: methylphenylsilicon grafted; film thickness: 0.4 μm ; length = 10 m, internal diameter = 100 μm) and a FID 40 flame ionization detector. Carbon dioxide was used as fluid vector. The general chromatographic conditions were established as follows: injection temperature = 40 °C, detector temperature = 320 °C and injection time = 200 ms. The chromatographic analyses were carried out at a constant temperature of 70 °C by using the following density programming:



2.1. Reaction between GMA and 1,4-butanediol

A mixture of 10 mmol of GMA, 5 mmol of BDO, 0.5 mmol of catalyst (10 mol% compared to BDO), and 0.4 g of dimethyltetraethyleneglycol (as internal reference) were introduced in a 25 ml Pyrex glass tube closed by a screwed joint of sealing covered with Teflon. The reaction mixture was magnetically stirred. Reactions were carried out in bulk or in a solvent (5 ml) in an oil bath thermostated at 40 °C for 24–72 h. Conversion of GMA, yields in 1,4-butanediyl dimethacrylate (BDMA) and 4-hydroxybutyl methacrylate (HBMA) were followed by SFC.

1,4-butanediyl dimethacrylate: ¹H-NMR (CDCl₃): δ 6.16 (m, 2H, H-CH=), 5.56 (m, 2H, H-CH=), 4.19 (m, 4H, -CH₂-O-), 1.95 (m, 6H, CH₃-C=), 1.80 (m, 4H, CH₂-CH₂-O-); ¹³C-NMR (CDCl₃) δ 127.3 (CH₂=), 139 (-C=), 170 (-C(O)O-), 66.7 (-CH₂-O), 27.7 (-CH₂-), 19.6 (CH₃-).

4-hydroxybutyl methacrylate: ¹H-NMR (CDCl₃): δ 6.10 (m, 1H, H-CH=), 5.56 (m, 1H, H-CH=), 4.19 (t, 2H, -CH₂-O), 3.69 (t, 2H, -CH₂-OH), 1.94 (m, 3H, CH₃-C=), 1.70 (m, 4H, -CH₂-CH₂-O-); ¹³C-NMR

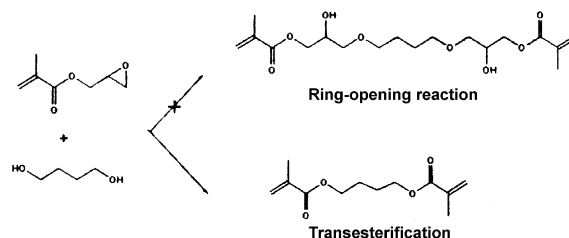
(CDCl₃) 125.4 (CH₂=), 136.4 (-C=), 18.3 (CH₃-), 167 (-C(O)O-), 64.5 (-CH₂-O-), 62.3 (-CH₂-OH), 29.2, 25.4 (-CH₂).

3. Results and discussion

3.1. Characterization of the reaction mechanism

During a preliminary study, the reaction was tested with various well-known oxirane ring-opening catalysts such as tetracyanoethylene (TCNE) [4], ceric ammonium nitrate (CAN) [5], and triethylamine (TEA) [6]. Reactions were carried out in bulk at 40 °C.

In the presence of CAN, a violent reaction leading to the formation of a polymer (even at 3 °C) characterized by the disappearance of the protons of methacrylate carbon-carbon double bonds (¹H-NMR: δ 6.17 and 5.61 ppm) was observed. The same result was obtained in acetone at 25 °C. In these conditions, CAN initiates a polymerization reaction involving the methacrylate groups. In presence of 5% TCNE compared to BDO, a decrease of about 30% of the glycidyl proton signals (δ 4.48, 4.01) is noticed on the ¹H-NMR spectrum. The reaction carried out in the presence of TEA is totally different to that in the presence of TCNE. With a TEA concentration of about 1%, a decrease of the glycidyl protons signal of more than 85% is noticed on the ¹H-NMR spectrum of the crude product. It has totally disappeared when the TEA concentration is 10%. However, ¹H-NMR analysis of the crude mixture is complicated by the presence of a broad signal at δ 3.5–4.1 ppm. To better investigate the reaction catalyzed by TEA, it was studied in various solvents (THF, acetone, and dioxane). Based on HPLC analysis, it was found that the formation of by-products is the lowest in THF. A preparative HPLC was performed to characterize the reaction products. The ¹H and ¹³C-NMR analyses of the isolated fractions showed the formation of HBMA, BDMA, and a mixture composed of BDO (¹³C-NMR: δ 61 and 29 ppm) and glycidol (¹H-NMR: δ 4.48 (dd) and δ 4.01 (dd) ppm).



Consequently, the reaction which really occurs is a transesterification. As previously reported [6], the transesterification can be catalyzed by TEA. To verify if the same reaction can occur with other methacrylate

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