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SYNTHESIS AND CHARACTERIZATION OF 3-CYCLOHEXYLOXY-2-HYDROXYPROPYL ACRYLATE AND ITS HOMOPOLYMER

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ABSTRACT

3-Cyclohexyloxy-2-hydroxypropyl acrylate was prepared from acrylic acid, cyclohexanol and epichlorohydrin. Polymerization of the monomer was carried out in 1,4-dioxane solution in presence of benzoyl peroxide as initiator. The monomer and the polymer microstructure were investigated by ^1H and ^{13}C nuclear magnetic resonance (NMR) and infrared techniques. Some properties of the homopolymer were also determined.

INTRODUCTION

Poly(hydroxyalkyl acrylates and methacrylates) are widely used in various branches of industry, particularly as a bio-material in surgery [1-3], as an aqueous phase dispersant, flocculant, and heat exchanger scale reducer in other fields[4]. Although there are many studies on the polymers of 2-

hydroxyethyl acrylates and methacrylates in literature [5-8], there are no more studies on the polymers of 2-hydroxypropyl acrylates and methacrylates[4,9].

This article presents the synthesis and characterization of 3-cyclohexyloxy-2-hydroxypropyl acrylate monomer and its homopolymer. They were also studied on thermal and solubility characteristics of the homopolymer.

EXPERIMENTAL

Materials:

Cyclohexanol (Merck) was reacted with a little amount of natrium, then was distilled under vacuum. Toluene, epichlorohydrin, pyridine, 1,4-dioxane, and acrylic acid (Aldrich) were freshly distilled before use. Diethyl ether, n-heptane, t-butanol, acetonitrile, nitromethane, ethanol and petroleum ether (Aldrich) were used as received.

Preparation of 3-cyclohexyloxy-2-hydroxypropyl acrylate(HHPA):

First, 1-cyclohexyloxy-3-chloro-2-propanol was synthesized from cyclohexanol and epichlorohydrin, and then 1-cyclohexyloxy-2,3-epoxypropane was obtained from this chlorhydrin compound via the method reported in the literature [10]. The monomer was prepared according to the method given for the epoxy-carboxy reactions [11,12]. 27 g (173 mmol) 1-cyclohexyloxy-2,3-epoxypropane and 25 g (347 mmol) acrylic acid was stirred in 150 ml toluene at 85°C under reflux condenser for 24 h in presence of 5.4 g (68 mmol) pyridine and 100 ppm hydroquinone as catalyst and inhibitor, respectively. Then the solution was cooled to the room temperature and was neutralized with dilute solution of NaHCO_3 . The organic layer was washed with water three times, and the water layer was washed with diethyl ether a few times. The

organic layers were collected, dried over anhydrous MgSO_4 . 3-cyclohexyloxy-2-hydroxypropyl acrylate(HHPA) was distilled at 130-132°C at 4 mmHg in presence of a small amount of hydroquinone (Yield: 65%, 25 g). Relative density of the monomer was measured as 1.0759 using a pycnometer. $n_{20} = 1.4744$, the results of elemental analysis: 62.91%C and 8.7 % H (Calc. 63.16%C and 8.77%H).

Polymerization of the HHPA monomer:

HHPA was freed from inhibitor by washing with 5% KOH solution followed by distilled water, drying over anhydrous MgSO_4 . Polymerization was carried out in 1,4-dioxane solution(monomer/solvent = 1/5, v/v) at 60°C using 0.2% benzoyl peroxide initiator. Appropriate amounts of HHPA and 1,4-dioxane were mixed in a reaction tube and purged with argon for 10 min. After the sealed tube had been kept at required temperature, the contents were poured into a large excess of petroleum ether. Poly(3-cyclohexyloxy-2-hydroxypropyl acrylate)(PHHPA) was purified by repeated precipitation by petroleum ether from solution in 1,4-dioxane and finally dried under vacuum.

Characterization techniques:

Infrared(IR) analysis was performed using a Py-Unicam SP 3.100 spectrophotometer. The ^1H and ^{13}C NMR spectra of the monomer and the homopolymer were recorded at 25°C with d_6 -dioxane as solvent for the polymer and d-chloroform as solvent for the monomer using a Varian-Gemini 200 MHz spectrometer. Thermal data were obtained using Shimatsu DSC-50 instrument and TG-50 thermo-balance. Average molecular weights were obtained by the gel-permeation chromatography(GPC) technique. Solubility parameter of the homopolymer was obtained from swelling measurements which were

Table 1. ^1H and ^{13}C NMR assignments for HHPA monomer

	1	2	3	4	5	6	7	8	9	10
^1H NMR(ppm)	6.42(H_A) ^a 5.82(H_X) ^a	6.15(H_B) ^a		4.25	4.00	3.50	3.25	1.90 ^b (1.10-1.40)	1.70 ^c	1.5
^{13}C NMR(ppm)	131.6	128.6	166.7	78.6	69.4	69.0	66.2	32.5	24.3	26.2

^aABX system ($J_{\text{AB}}=17.0\text{Hz}$, $J_{\text{BX}}=10.3\text{Hz}$, $J_{\text{AX}}=1.7\text{Hz}$), ^baxial protons, ^cequatorial protons

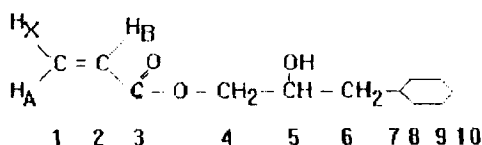


Figure 1. key to position numbering in table or in text.

performed at 20°C , and from the solubility test using 1,4-dioxane as solvent, n-heptane and nitromethane as non-solvents. Density of the polymer was determined in mixtures of formic acid and methanol using floatation method.

RESULTS AND DISCUSSION

Signal assignments of ^1H and ^{13}C NMR spectra of the HHPA monomer are shown in Table 1 according to the key in Fig 1.

The IR spectrum of the monomer shows characteristic bands at 3300cm^{-1} (broad) for OH group, at 1710cm^{-1} for carbonyl in ester and at 905cm^{-1} , 990cm^{-1} for vinyl group.

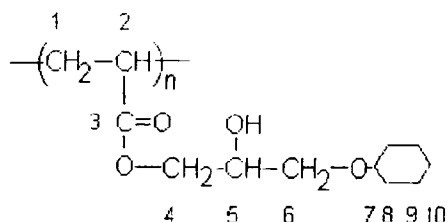


Figure 2. key to position numbering in text.

The ^1H and ^{13}C NMR spectra of the homopolymer are shown in Figures 3a and 3b. The signals at 3.2-4.1 ppm are assigned to $\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OCH}$ and d_8 -dioxane. The signals of methine protons in polymer backbone are at 2.1-2.6 ppm. Proton resonances of cyclohexane ring, except methine proton, are at 1.1-2.0 ppm. The signals of methylene protons in the backbone are probably under those of cyclohexane ring protons. ^{13}C NMR assignments according to the key in Fig.2 (solvent : d_8 -dioxane), in ppm :

$\delta = 179.6, 179.5(\text{C}_3) ; 82.5(\text{C}_4) ; 74.5(\text{C}_5) ; 73.4(\text{C}_6) ; 72.1, 71.5(\text{C}_7) ; 46.3(\text{C}_1) ; 45.9, 44.8(\text{C}_2) ; 37.4(2\text{C}_8) ; 31.1(\text{C}_{10}) ; 29.1(2\text{C}_9)$

The resonances of C_1 and C_2 carbons were estimated from among the signals of d_8 -dioxane by aid of peak intensities in computer data.

The GPC system calibrated with polystyrene in tetrahydrofuran(THF) showed that the weight-average molecular weight of the PHHPA was 8097 (polydispersity 3.68).The DSC curve shows a glass transition temperature at around 8°C for PHHPA. This value is higher than that of polypropyl acrylate($T_g = -49^\circ\text{C}$)[13] because of etheric and hydroxyl side groups in the PHHPA. These side groups cause the formation of inter and intramolecular hydrogen bonding. The thermogram of PHHPA is compared with that of poly(*p*-biphenyl acrylate)(PBA) [14] in Fig. 4. The

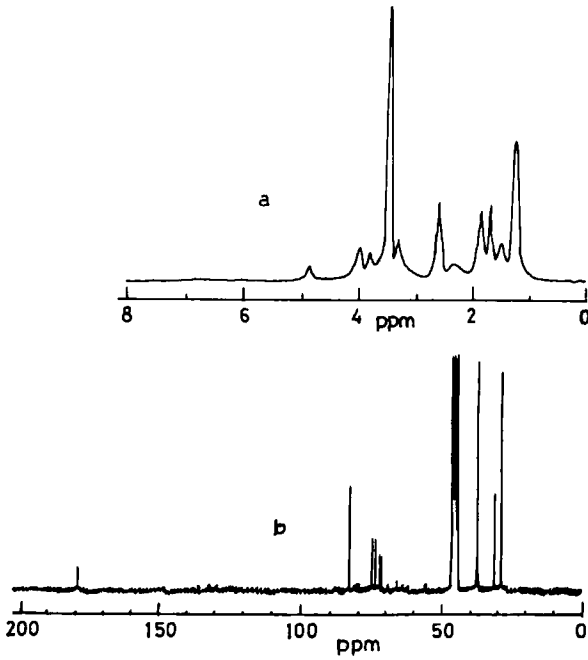


Figure 3. a) ^1H NMR spectrum and b) ^{13}C NMR spectrum of poly(HHPA)
Solvent : d_8 -dioxane

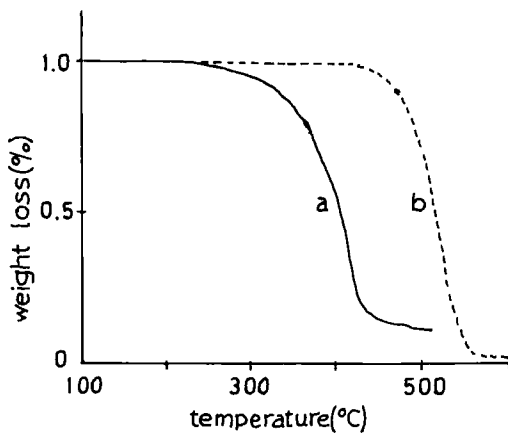


Figure 4. TGA curves of (a) poly(HHPA), (b) poly(BPA)[14].

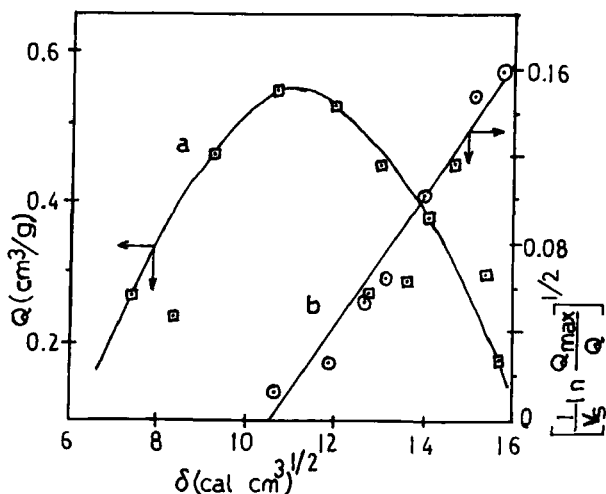


Figure 5. a) Plot of swelling coefficients(Q) versus solubility parameters(δ) and (b) plot of computation of solubility parameter for poly(HHPA)

degradation of PHHPA, except at 160-260°C, appeared at two stages. The first stage was observed at 260-415°C, the second stage by which the weight loss rate was higher than that of the first stage, was at 415-450°C, however, the PBA shows single stage degradation at 350-550°C. The TGA of PHHPA showed that the weight loss at 405°C was 50%. The residue at 450°C, at which point the degradation was completed, was about 16.5%. It was not soluble in several solvents. This indicates that the crosslink occurred during the degradation.

Solubility parameter was determined from swelling measurements. The swelling coefficient (Q) is given by following equation [6] :

$$Q = Q_{\max} e^{-\frac{(\delta_s - \delta_p)^2}{V_s}}$$

Table 2. Solubility parameters(δ_s) and molar volumes(V_s) of solvents and mixture of solvents

Solvents and mixture of solvents ^a	$\delta_s(\text{cal}^{1/2}\text{cm}^{-3/2})^b$	$V_s(\text{cm}^3)^c$
n-heptan	7.40	146.55
3 n-heptane+ 2 t-butanol	8.35	125.52
1 n-heptane+2 t-butanol	9.21	111.32
t-butanol	10.60	93.97
acetonitrile	11.90	52.24
nitromethane	12.70	53.68
1 water + 3 t-butanol	13.02	52.20
1 water + 4 acetonitrile	13.60	40.23
1 water + 2 acetonitrile	15.30	33.42
1 water + 2 ethanol	15.70	35.72

^a Numbers in front of solvent are volume ratios.

^b Solubility parameters of mixtures were found by calculating.

^c Molar volumes of mixtures were found by calculating.

Where Q_{max} is the swelling coefficient in the maximum swelling and V_s is the molar volume of the solvent, and δ_s and δ_p solubility parameters for solvent and polymer, respectively. When δ_p is equal to δ_s , the maximum swelling of the polymer will occur. A plot of Q vs δ_s will give a Gaussian curve. But a plot of $\{(1/V_s)[\ln Q_{\text{max}}/Q]\}^{1/2}$ vs δ_s will give a straight line. The corresponding plots are in Fig.5. Solubility parameters (δ_s) and molar Volumes(V_s) of the solvents and the mixture of solvents used as swelling agent are shown in Table 2. The solubility parameter was found as $10.4 \text{ cal}^{1/2}\text{cm}^{-3/2}$ from the plots and as $10.1 \text{ cal}^{1/2}\text{cm}^{-3/2}$ from solubility test using 1,4-dioxane as solvent, n-heptane and nitromethane as non solvent, according to the method adapted from literature [15]. There is a good agreement between values obtained by these two methods.

The density of the polymer was determined as 1.13 gcm^{-3} by the floatation method [15] using mixtures of methanol and formic acid as the floating agent, and lots of glass beads of known densities.

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