Synthesis and Characterization of Crosslinked Polyacrylates Containing Cubane and Silyl Groups

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Abstract: Attaching the organosilyl groups to macromolecular chains of 2-hydroxyethyl methacrylate (HEMA) should lead to important modifications of polymer properties. *t*-BuMe$_2$Si and cubane-1,4-dicarboxylic acid (CDA) were covalently linked with 2-hydroxyethyl methacrylate (HEMA). The silyl-linked HEMA is abbreviated as TSMA, while cubane-1,4-dicarboxylic acid (CDA) linked to two HEMA groups is the cross-linking agent (CA). Free radical cross-linking copolymerization of TSMA and HEMA with various ratios of CA as the cross-linking agent was carried out at 60-70 °C. The compositions of the cross-linked, three-dimensional polymers were determined by FTIR spectroscopy. The glass transition temperature (T_g) of the network polymers was determined calorimetrically. The T_g of the network polymer increased with increasing cross-linking degree.

Keywords: copolymerization, cross-linking, glass transition temperature, silyl group, modified polymer.

Introduction

The combination of versatility and tailored molecules has relatively easily made acrylic and methacrylic esters prime candidates for diverse applications.[1-7] Polymers containing organosilyl groups are an interesting research field in polymer and silicon chemistry. Attaching the organosilyl groups to macromolecular chains should lead to important modifications of polymer properties such as gas permeability and permselectivity parameters, mechanical, thermal, and surface properties, as well as photochemical reactivity.[8-16] These polymers usually showed high oxygen permeability and a reasonably high permselectivity of oxygen against nitrogen. The permeability behavior was attributed to a high affinity of oxygen molecules to Si atoms and the relatively large free volumes between the polymers, resulting from the restricted mobility of the side chains in the repeat units.[17] Nagasaki *et al*. reported that the oxygen permeability coefficient (PO$_2$) of the organosilicone-containing polymer membranes increased with the Si content.[18,19] The increased oxygen permeability was attributed to the empty d-orbital of Si atom, which interacts with oxygen molecule. They founded that the mobility of the side chains also strongly influenced the gas permeability of the polymer membranes since the restricted movements in the side chains increased the free volume.

In the present work, we report the synthesis and properties of 2-hydroxyethyl methacrylate (HEMA) polymers modified with *t*-BuMe$_2$Si group. The methacryloyloxyethyl ester of *t*-BuMe$_2$Si (TSMA) and cubane-1,4-dicarboxylic acids were prepared as polymerizable silylmonomer and cross-linking agent (CA), respectively. Free radical cross-linking copolymerization of the TSMA and HEMA with the various CA ratios produced silyl pendent network polymers. The DSC analysis showed that the attaching of silyl group in copolymer reduces the T_g value. Influences of different factors such as cross-linking and attaching silyl group studied.

Experimental

Synthesis of monomers and copolymerization were carried out under dry argon to exclude oxygen and moisture from the reaction systems.

Materials. Cubane-1,4-bis(methacryloyloxyethyl) carboxylate (CA) was prepared by the method described in the literature.[20] The solvents and reagents were purchased from Merck and Fluka Co. THF was dried by standard method and *t*-BuMe$_2$SiCl used as received. Initiator of, α,α'-azobis (isobutyronitrile) (AIBN) was purified by crystallization from methanol.

Measurements. ^{1}H-NMR spectra were recorded on a Brucker 400 AC spectrometer in CDCl$_3$ and DMSO-d$_6$. The IR spectra were recorded on a Shimadzu FT IR-408 spectrophotometer. The DSC curves were obtained on a TGA/SDTA 851 calorimeter at heating and cooling rates of 10 °C/

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min in air. The molecular weights (M_w and M_n) were determined by using a Waters 501 gel permeation chromatograph fitted with 102 and 103 nm Waters Styragel columns. THF and DMF were used as elution solvents at a flow rate of 1 mL/min and polystyrene standards were employed for calibration.

Monomers Synthesis.

2-Propenoiec acid, 2-methyl-2-[(t-butyldimethyl silyl) oxy] ethyl ester (TSMA): A mixture of 3 g (23 mmol) HEMA and 3.5 g (34 mmol) triethylamine in 50 mL dried THF was treated in a drop wise manner with a solution of 3 g (23 mmol) t-butyl dimethylchlorosilane in 10 mL dried THF under dry argon at room temperature. After 24 h stirring at room temperature the reaction mixture was filtered. The THF was removed under reduced pressure to produce a nearly colorless oily residue. The residue was chromatographed over silica gel by CH_2Cl_2 to yield (25%) of TSMA. IR (neat, cm^{-1}): 2985, 2930, 1722, 1257, 837, 1131, 1168. ^{1}H-NMR ($CDCl_3$, ppm): 0.06 (s, 6H, -CH_3), 0.8 (s, 9H, t-Bu), 1.9 (s, 3H, -CH_3), 3.8 (t, 2H, -OCH_2), 4.2 (t, 2H, -$COOCH_2$), 5.5 (s, 1H, CH_2=), 6.1 (s, 1H, CH_2=).

Synthesis of Poly(HEMA-co-TSMA, 1:1). In two Pyrex glass ampoules, a mixture of 0.52 g (4 mmol) of HEMA, 0.05 g (0.3 mmol) of AIBN and 1 g (4 mmol) of TSMA, was dissolved in 25 mL of dioxane. Then the ampoule was degassed, sealed under vacuum and maintained at 70 °C in a water bath and shaken by a shaker machine for about 24 and 72 h. Then the viscous solutions were poured from the

ampoule into 150 mL of cooled water, the precipitates were collected and dried under vacuum at room temperature to give 1 g of copolymer I (yield: 68%) with reaction time 24 h and 1.3 g of copolymer II (yield: 86%) with reaction time 72 h. ^{1}H-NMR ($CDCl_3$, ppm): 0.03-0.07 (broad, CH_3), 0.7-1.7 (broad, CH_3 of t-Bu & CH_2 of chain), 3.7 (broad, CH_2O), 3.9 (broad, CH_2O), 4.8 (broad, OH). FTIR (KBr, cm^{-1}): 3448, 2955, 1730, 1258, 837.

Cross-linked Copolymerization. In two Pyrex glass ampoules, a mixture of 1 g (4 mmol) of TSMA, 0.52 g (4 mmol) of HEMA and specific mol percents of CA (5 and 10%) were polymerized at 60-70 °C in a thermostatic water bath, using 2,2-azobisisobutyronitrile (AIBN) as initiator ($[I]$= 0.02 M), and dried dioxane as solvent ($[M]$=1.0 M). After the specified time (72 h), the precipitated network polymer was collected, washed with methanol and dried in vacuum. The yields of polymers are 89 and 91%, respectively (Scheme I).

Results and Discussion

For synthesis of new modified polymers, we used two methods: copolymerization and cross-linked copolymerization. In copolymerization, the TSMA monomer was copolymerized with HEMA (1:1) in dioxane at 70 °C using AIBN as the radical polymerization initiator at two reaction time. Gel permeation chromatography (GPC) was used to determine the number and weight-average molecular weights of
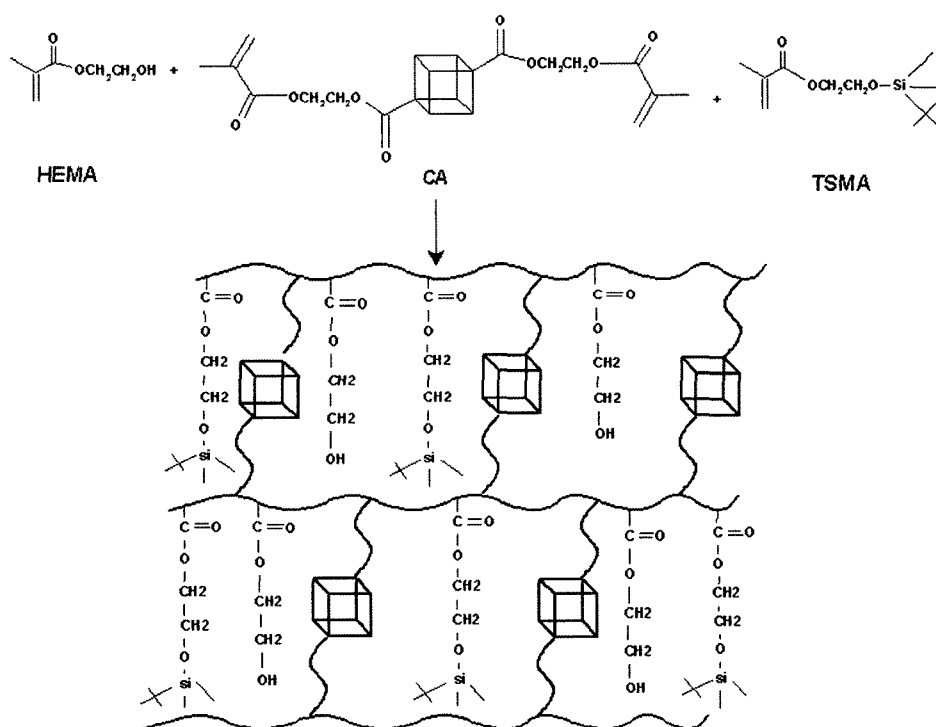
Scheme I. Preparation of cross-linked copolymers containing silyl group.

Table I. The Molar Compositions, DSC and GPC Data of Copolymers

Copolymer	Molar Composition of Monomers in the Feed HEMA and TSMA	Percent of CA	Time/h	% mole HEMA	% mole TSMA	Yield in %	M_w/M_n	M_w	$T_g(^\circ C)$	IDT $(^\circ C)$	PDT$_{max}$ $(^\circ C)$
I	1:1	-	24	80	20	68	1.38	6443^a	85	260	295
II	1:1	-	72	65	35	86	1.97	37564^b	55	270	310
III	1:1	5	72	---	---	89	-	-	150	240	265
IV	1:1	10	72	---	---	91	-	-	180	255	270

^{a}Determined by GPC with DMF eluent. ^{b}Determined by GPC with THF eluent.

copolymers and the results are listed in Table I. The resulted copolymers (I and II) are white solids and their solubility reported in Table II.

The copolymer compositions were calculated from the ^{1}H-NMR spectra data. In the past few decades ^{1}H-NMR spectroscopic analysis has been established as a powerful tool for the determination of copolymer compositions because of its simplicity, rapidity and sensitivity.[21] Spectrum of copolymer I in DMSO-d$_6$ is shown in Figure 1. The molar compositions of HEMA and TSMA in copolymer I were calculated from the ratio integrated intensities of the peaks around 0.03-0.07 ppm, corresponding of six protons of methyl in TSMA units to the total area between 0.4-2.2 ppm, which were attributed to nineteen protons marked by (#) in HEMA and (*) in TSMA, respectively.

Table II. The Solubility of Copolymer

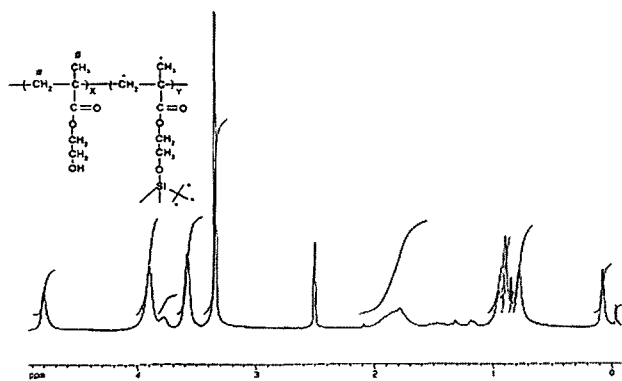| Solvent	I	II
Chloroform	-	+
THF	-	+
Water	-	-
DMF	+	+
Acetone	+	+
Methanol	+	+

+ Soluble, - insoluble.

Figure 1. 400 MHz ^{1}H-NMR spectrum of copolymer I in DMSO-d$_6$.

The molar compositions of HEMA and TSMA were calculated from eqs. (1) and (2) where x and y were the mole fractions of HEMA and TSMA, respectively.

$$\frac{\text{Area at } 0.03-0.07\text{ppm}}{\text{Area at } 0.4-2.2\text{ppm}} = \frac{6x}{14x+5y} \quad (1)$$

$$x+y = 1 \quad (2)$$

A similar method was used to calculate the molar composition of copolymer II. The composition of copolymer is presented in Table I. As shown in Table I, the low reactivity ratio of TSMA in copolymers, perhaps related to steric effect of bulky silyl group in TSMA, which that reduce, of reactivity. With increasing of time reaction molar composition of TSMA increased.

Identification of Network Polymer. The resulting network polymers swell and become soft if they are exposed to solvents such as H$_2$O and most organic solvents without dissolving. In the FTIR spectra, absorption of C-Si bond appeared in of 1258 and 837 cm^{-1} that is referring to stretching, and bending vibration, respectively.

Thermal Behaviour. Among polycyclic hydrocarbons, cubane (penta cyclo [4. 2. 0. 02, 5.03, 8.04, 7] octane) holds a particular fascination, both because of its symmetry and also its highly strained structure. Because the cubane frame is a rigid one, its substituents have precise spatial relationships to one another.[21] In general, polymers having low glass transition temperature show high diffusion coefficients for small molecules, but polymers having high glass transition temperature, exhibit a considerably higher permselectivity. Differential scanning calorimetry (DSC) and thermal gravimetry (TGA) for the network polymers were evaluated. The thermal properties of the polymers are summarized in Table I, including the T_g of the polymers, initial decomposition temperature of the polymer (IDT) and also the temperature at which the maximum decomposition rate occurred for the polymers (PDT$_{max}$). It appears that with increased cross-linking degree, which would decrease the flexibility of the chains and the ability of the chains to undergo segmental motion, which would increase the T_g values.[20,23] Cubane has the highest strain energy (166 Kcal/mol) of any organic compounds available in multi gram amount. It is a kinetically

stable compound and only decomposite above 220 Celsius Degree. Because in cross-linking polymers with cubane derivatives as a cross-linking agent, decomposition occurred about 230-270 °C. The T_g value of the homopolymer[22] without the silyl group would be higher than T_g value of the copolymers. The silyl group not only reduced of internal hydrogen bonds between the polymer chains but also as a plasticizer increases the flexibility of hard polymers and reduces it's T_g.

Conclusions

The copolymer and cross-linked copolymers were synthesized by free radical copolymerization. The DSC analysis indicated that the glass transition temperature of copolymer decreases with incorporation of silyl groups in side chains of polymer. With incorporation of silyl groups, the solubility of polymethacrylate was increased. Polymethacrylates dissolved difficulty in many solvents. This effect can be an important case in industrial procedures. Therefore, placing silyl groups and regulating the cross-linking degree can produce us the novel polymer systems with the new physical and chemical properties and new applications. The polymers with silyl groups have been used as a membrane before; therefore we expect these polymers also possess membrane properties.

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