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Synthesis and characterization of some organosilicon derivatives of poly 2-hydroxyethyl methacrylate with cubane as a cross-linking agent

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Abstract

Some silyl ether derivatives of 2-hydroxyethyl methacrylate (HEMA) were prepared. The Et_3Si, Ph_3Si and Me_3Si groups together with cubane-1,4-dicarboxylic acid (CDA) were covalently linked with HEMA. The silyl-linked HEMA are abbreviated as TETMA, TPhMA and TMEMA, respectively. CDA linked to two HEMA groups is the cross-linking agent (CA). Free radical copolymerization and cross-linking copolymerization of the resulting monomers with 2-hydroxyethyl methacrylate (HEMA) with the various ratios of CA as cross-linking agent, were carried out using AIBN as initiator at the temperature ranges 60–70 °C. The cross-linking copolymers were identified by FT-IR spectroscopy. The glass transition temperature (T_g) of the network polymers was determined calorimetrically. The T_g of network polymers increases with increase of cross-linking degree. All monomers and polymers were identified by spectroscopic methods. These silyl derivatives modified methacrylate polymer properties.

Keywords: Cross-linking; Silyl group; Copolymerization; Cubane

1. Introduction

Attaching the organosilyl groups to macromolecular chains as a 2-hydroxyethyl methacrylate (HEMA) polymer should lead to important modifications of polymer properties. The combination of versatility and tailored molecules has relatively easily made acrylic and methacrylic esters prime candidates for diverse applications. 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 perm selectivity parameters, mechanical, thermal and surface properties, as well as photochemical reactivity [1–8]. On the other hand, some silyl derivatives of polymers such as acrylates and styrene showed membrane properties [9]. One of the important properties of these membranes is selectivity with reference to oxygen. The membrane usually showed high oxygen permeability and a reasonably high perm selectivity of oxygen against nitrogen and carbon dioxide. 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 chain in the repeat units. Thus, this type of polymers may be applicable to the biosensor electrode membrane as their chemical and physical properties are appropriate. In this way, silyl methacrylate was also used in contact lens. These lenses with silyl chain have

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interesting properties with reference to polymer without the silyl group. The selectivity of organosilicon methacrylates with reference to oxygen is an important factor in these properties, where some silyl derivatives of methacrylate polymers used in contact lens were patented. On the other hand, silyl methacrylates have been extensively used in photolithographic applications [10]. A process for producing a controlled drug-release contact lens, containing a first member which forms a front fact of the lens and a second member which forms a rear face of the lens, the first and second members defining a space in the contact lens, which entails (a) preparing the first and second members from a non-cross-linked polymer; (b) bonding the prepared first and second members by melt pressing; and (c) cross-linking the bonded members by hydration treatment, wherein the non-cross-linked polymer is obtained from a polymerizable methoxy silicone compound and another monomer copolymerizable therewith [11]. For these reasons in the present work, we report the synthesis and properties of 2-hydroxyethyl methacrylate (HEMA) polymers modified with some silyl groups. The methacryloyloxyethyl ester of Et_3Si, Me_3Si, and Ph_3Si was synthesized and polymerized with HEMA. Free radical cross-linking copolymerization of the silyl derivatives of 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 were studied.

2. Experimental

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

3. Materials

Cubane-1,4-bis(methacryloyloxyethyl)carboxylate (CA), was prepared by the method described in the literature [12]. The solvents and reagents were purchased from Merck and Fluka Co. Et_3SiCl, Me_3SiCl, and Ph_3SiCl were used as received. Initiator of α,α′-azobis(isobutyronitrile) (AIBN) was purified by crystallization from methanol.

3.1. Measurements

^1H NMR and ^{13}C NMR spectra were recorded on a Brucker 400 AC spectrometer in $CDCl_3$. The IR spectra were recorded on a Shimadzu FT IR-408 spectrophotometer.The DSC curves was obtained on a TGA/SDTA 851 calorimeter at heating and cooling rates of 10 °C/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 was used as an elution solvent at a flow rate of 1 ml/min and polystyrene standards were employed for calibration.

4. Monomers synthesis

4.1. 2-Propenoic acid, 2-methyl-2-[(triphenylsilyl)oxy]-ethyl ester (TPhMA)

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 6.7 g (23 mmol) triphenylchlorosilane in 10 ml dried THF under dry argon at room temperature. After (3 h) stirring at room temperature the reaction mixture was filtered. Then 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 35% of TPhMA. IR (neat, cm^{-1}): 2985, 2930, 1722, 1257, 837, 1131, 1168. ^1H NMR ($CDCl_3$, ppm): 1.95 (s, 3H, $–CH_3$), 4.06 (t, $J = 4$ Hz, 2H, $–CH_2O$), 4.35 (t, $J = 4$ Hz, 2H, $–COOCH_2$), 5.57 (m, 1H, $=CH_2$), 6.10 (m, 1H, $=CH_2$), 7.39–7.68 (m, 15H, phenyl-H). ^{13}C NMR ($CDCl_3$, ppm): 17.10 ($–CH_3$), 60.80 ($–CH_2O$), 64.48 ($–COOCH_2$), 124.46 ($=CH_2$), 134.94 (=C), 166.10 (–COO), 126.73, 128.52, 132.58, 134.14 (C-phenyl). m/z (EI) : 388 $(M)^+$ (6%), 311 (95%), 105 (90%).

4.2. 2-Propenoic acid, 2-methyl-2-[(triethylsilyl)oxy]-ethyl ester (TETMA)

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 3.5 g (23 mmol) triethylchlorosilane in 10 ml dried THF under dry argon at room temperature. After (6 h) stirring at room temperature the reaction mixture was filtered. Then THF was removed under reduced pressure to produce a nearly colorless oily residue. The residue was purified by chromatographic method over silica gel by CH_2Cl_2 to yield 35% of TETMA. IR (neat, cm^{-1}): 2955, 1722, 1241, 814. ^1H NMR ($CDCl_3$, ppm): 0.54–0.60 (q, $J = 8$ Hz, 6H, $–SiCH_2$), 0.90–0.94 (t, $J = 8$ Hz, 9H ($–CH_3$ of ethyl ($CH_3–CH_2Si$), 1.91 (s, 3H, $–CH_3$), 3.81 (t, $J = 4$ Hz, 2H, $–CH_2O$), 4.19 (t, $J = 4$ Hz, 2H, $–COOCH_2$), 5.52 (m, 1H, $=CH_2$), 6.09 (m, 1H, $=CH_2$). ^{13}C NMR ($CDCl_3$, ppm): 4.30 ($–SiCH_2$), 6.63 ($–CH_3$ of ethyl ($CH_3–CH_2Si$)), 18.31 ($–CH_3$), 60.90 ($–CH_2O$), 65.93 ($–COOCH_2$), 125.53 ($=CH_2$), 136.23 (=C), 167.49 (–COO). m/z (EI): 215 $(M – Et)^+$(18%), 171 (26%), 143 (10%), 115 (15%).

5. 2-Propenoic acid, 2-methyl-2-[(trimethylsilyl)oxy]ethyl ester (TMEMA)

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 2.5 g (23 mmol) trimethylchlorosilane in 10 ml dried THF under dry argon at room temperature. After (5 h) stirring at room temperature, the reaction mixture was filtered and the solvent 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 35% of TMEMA. IR (neat, cm^{-1}): 2959, 1721, 1252, 843. ^1H NMR ($CDCl_3$, ppm): 0.19 (s, 6H, $-SiCH_3$), 2.02 (s, 3H, $-CH_3$), 3.90 (t, $J = 4$ Hz, 2H, $-CH_2O$), 4.29 (t, $J = 4$ Hz, 2H, $-COOCH_2$), 5.64 (m, 1H, $=CH_2$), 6.20 (m, 1H, $=CH_2$). ^{13}C NMR ($CDCl_3$, ppm): 2.30 ($-SiCH_3$), 18.35 ($-CH_3$), 60.88 ($-CH_2O$), 65.90 ($-COOCH_2$), 125.40 ($=CH_2$), 136.10 (=C), 167.30 (–COO). *m/z* (EI): $187(M - Me)^+$(10%), 143 (20%), 116 (15%), 103 (20%).

6. Polymer synthesis

6.1. Synthesis of poly(HEMA-TMEMA, 1:1) (I)

In a Pyrex glass ampoule, a mixture of 0.52 g (4 mmol) of HEMA, 0.02 g (0.01 M) of AIBN and 0.80 g (4 mmol) of TMEMA was dissolved in 25 ml of dioxane. Then the ampoule was degassed, sealed under vacuum and started to polymerization at 60–70 °C, with stirring, for about 72 h. Then the viscous solution was poured from the ampoule in to 150 ml of cold water, the precipitate was collected and dried under vacuum at room temperature to give 0.2 g of copolymer. IR (neat, cm^{-1}): 3440 2954, 1732, 1264, 900. ^1H NMR ($CDCl_3$, ppm): 0.71 (s, $-SiCH_3$), 0.92–1.98 (b, CH_2,CH_3), 3.58–3.96 ($-CH_2O$, $-COOCH_2$), 4.86 (b, 1H, OH).

6.2. Synthesis of poly(HEMA-TPhMA, 1:1) (IV)

In a Pyrex glass ampoule, a mixture of 0.52 g (4 mmol) of HEMA, 0.02 g (0.01 M) of AIBN and 1.55 g (4 mmol) of TPhMA was dissolved in 25 ml of dioxane. Then the ampoule was degassed, sealed under vacuum and started to polymerize at 60–70 °C, with stirring for about 72 h. Then the viscous solution was poured from the ampoule into 150 ml of cold heptane, the precipitate was collected and dried under vacuum at room temperature to give 0.2 g of copolymer. IR (neat, cm^{-1}): 3444, 3053, 2945, 1727, 1589, 1486, 1266, 873. ^1H NMR ($CDCl_3$, ppm): 0.87–1.85 (b, CH_3, CH_2), 2.89 (b, 1H, OH), 3.71–3.96 ($-CH_2O$, $-COOCH_2$), 7.27–7.66 (m, 15H, phenyl-H).

6.3. Synthesis of poly(HEMA-TETMA, 1:1) (VII)

In a Pyrex glass ampoule, a mixture of 0.52 g (4 mmol) of HEMA, 0.02 g (0.01 M) of AIBN and 1.00 g (4 mmol) of TETMA was dissolved in 25 ml of dioxane. Then the ampoule was degassed, sealed under vacuum and started to polymerize at 60–70 °C, with stirring, for about 72 h. Then the viscous solution was poured from the ampoule in to 150 ml of cold water, the precipitate was collected and dried under vacuum at room temperature to give 0.2 g of copolymer. IR (neat, cm^{-1}): 3440 2954, 1730, 1273, 801. ^1H NMR ($CDCl_3$, ppm): 0.60–1.13 ($-SiCH_2-CH_3$), 1.78–1.87 (b, CH_2, CH_3), 3.57–3.89 ($-CH_2O$, $-COOCH_2$), 4.81 (b, 1H, OH).

7. Cross-linking polymerization

7.1. Cross-linked copolymerization of TETMA and HEMA with CA (VIII, IX)

In two Pyrex glass ampoules, a mixture of 1 g (4 mmol) of TETMA, 0.52 g (4 mmol) of HEMA and specific mol percentage of CA (5% and 10%) was polymerized at 60–70 °C in a thermostatic water bath, using 2,2-azobisisobutyronitrile (AIBN) as initiator ($[I] = 0.01$ M), and dried dioxane as solvent ($[M] = 1.0$ M). After the specified time (72 h), the precipitated network polymer (0.30 g) was collected, washed with methanol or water and dried in vacuum. IR (neat, cm^{-1}): 3540, 2952, 1730, 1264, 845.

7.2. Cross-linked copolymerization of TPhMA and HEMA with CA (V, VI)

In two Pyrex glass ampoules, a mixture of 1 g (2.6 mmol) of TPhMA, 0.4 g (2.6 mmol) of HEMA and specific mol% of CA (5% and 10%), in the presence of AIBN ($[I] = 0.01$ M) as initiator, and dried dioxane as solvent ($[M] = 1.0$ M) were polymerized at 60–70 °C in a thermostatic water bath. After the 72 h, the precipitated network polymer (0.28 g) was collected and washed with heptane and dried in vacuum. IR (neat, cm^{-1}): 3540, 2952, 1730, 1260, 845.

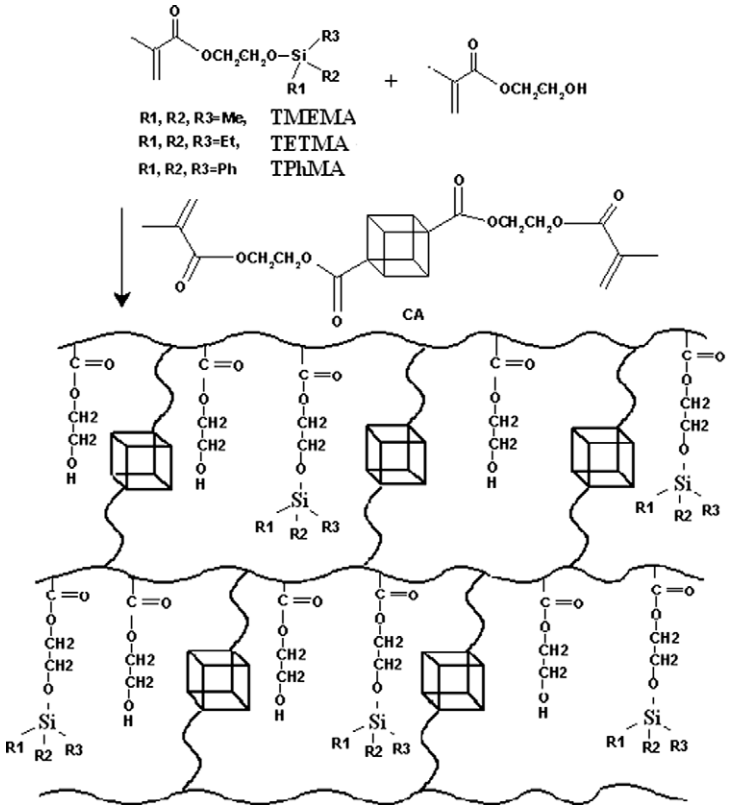
7.3. Cross-linked copolymerization of TMEMA and HEMA with CA (II, III)

In two Pyrex glass ampoules, a mixture of 1 g (5 mmol) of TMEMA, 0.65 (5 mmol) of HEMA and specific mol percentage of CA (5% and 10%), in the presence of 2,2-azobisisobutyronitrile (AIBN) as an initiator, and dried dioxane as solvent ($[M] = 0.1$ M) was polymerized at 60–70 °C in a thermostatic water bath. After 72 h, the precipitated network polymer (0.34 g)

was collected with methanol or water and washed with cold methanol and dried in vacuum. IR (neat, cm^{-1}): 3430, 2960, 1730, 1264, 850.

8. Results and discussion

In this work, we synthesized some organosilicon derivatives of HEMA, which Et_3Si, Me_3Si and Ph_3Si groups are as a side chain. These monomers were prepared by using Et_3SiCl, Me_3SiCl and Ph_3SiCl in the presence of Et_3N as a base in THF with 2-hydroxyethylmethacrylate. For synthesis of new modified polymers, we used two methods: copolymerization and cross-linked copolymerization. In copolymerization, the TMEMA, TETMA, and TPhMA monomer was copolymerized with HEMA in dioxane at 70 °C using AIBN as the radical polymerization initiator with a ratio of 1:1. In cross-linking copolymerization, cubane-1,4-dicarboxylic acid (CDA) linked to two 2-hydroxyethyl methacrylate (HEMA) group was used as a cross-linking agent (CA). Because the cubane frame is rigid, substituents have precise spatial arrangements to one another. The distance across the cube (the body diagonal) is almost the same as that between the *para* positions of a benzene ring. Due to their well-defined dimensionality and rigid geometry, cubane could prove to be important building blocks in the developing world of nanoarchitecture, in the form of oligomeric compounds and polymers. Although many physical properties of cubane have been measured, until about 10 years ago, cubane was considered just a laboratory curiosity of interest only to academics. Recently, however, the possible applications in industry, materials science, medicine and polymer have come to light. The copolymers were synthesized by free-radical polymerization. In this way, we synthesized cross-linked copolymer with HEMA and silyl derivatives by using cross-linking agent of cubane (CA) (Scheme 1). These copolymers were identified by DSC analysis and IR spectra. By regulating the cross-linking percentage of the silyl copolymers, we can improve polymer properties. Cubane are not inherently toxic. They are considered as biologically stable, lipophilic platforms on which a wide choice of substituents in a variety of well defined spatial relationships can be installed. Also, a cubane derivative has been known for its versatility and may be pharmaceutical basis for future application of cubane and its derivatives. In the recent research, we used copolymers of cubane as a carrier of some drugs, for example, indomethacine, ibuprofen, and olsalazine [9]. Gel permeation chromatography (GPC) was used to determine the number and weight-average molecular weights of copolymers and the result is listed in Table 1. The copolymer composition was calculated from the ^1H NMR spectra data. In the past few decades, ^1H NMR spectroscopic analysis has been



Scheme 1. Preparation of cross-linked polymers containing silyl group.

Table 1
DSC and GPC data of copolymers

Copolymer	Percent of CA	M_w	M_w/M_n	T_g (°C)
I	–	6589	1.36	95
II	5	–	–	138
III	10	–	–	150
IV	–	22,000	–	70
V	5	–	–	95
VI	10	–	–	105
VII	–	7138	1.43	100
VIII	5	–	–	120
IX	10	–	–	138

established as a powerful tool for the determination of copolymer compositions because of its simplicity, rapidity and sensitivity [13,14]. The molar composition of HEMA and silyl derivatives in copolymer was calculated from the ratio integrated intensities of the silyl protons refer to the protons of ethyl or hydroxyl groups. The molar composition of TPhMA and TETMA was calculated from the following equations, where x and y are the mole fractions of HEMA and TPhMA, TETMA, respectively [15] (see Table 2).

For TPhMA:

$$x + y = 100,$$

$$\frac{\text{Area at 7.2–7.6 ppm}}{\text{Area at 3.7–3.9 ppm}} = \frac{15y}{4x + 4y},$$

$$\frac{15}{6.8} = \frac{15y}{4x + 4y},$$

$$x = 41\%, \quad y = 59\%.$$

For TETMA:

$$\frac{\text{Area at 0.6–1.1 ppm}}{\text{Area at 3.5 ppm}} = \frac{15y}{2x + 2y},$$

$$\frac{4.4}{2} = \frac{15y}{2x + 2y},$$

$$x = 30\%, \quad y = 70\%.$$

The important effects of silyl groups is decreasing of T_g and increasing of solubility. Decreasing of T_g can cause increasing of polymer flexibility, and improve its properties. One of the important cases in polymer industry is solubility of them; therefore, we showed that attaching of silyl group to hydroxyethylmethacrylate could increase the solubility of them, in which that copolymer TETMA with HEMA was dissolved in

Table 2
The molar compositions of copolymers I, IV, VII

Copolymer	Ratio of monomers	Time/h	Percent of HEMA	Percent of silyl
I	1:1	72	40	60
IV	1:1	72	41	59
VII	1:1	72	30	70

Table 3
Solubility of polymers

Solvents	I	IV	VII
Acetone	+	+	–
CH_2Cl_2	–	+	–
THF	–	+	–
EtOH	+	–	+
DMF	+	–	+

+, soluble; –, insoluble.

EtOH, MeOH, and DMF (see Table 3). In addition to the above properties, in loading of drugs to polymers it has been shown that it is a balance between hydrophilic and lipophilicity of polymer. Since most of drug molecules have a lipophile structure, therefore, the presence of lipophile groups on the polymer chain increases drug loading. The silyl groups that we used in this work are lipophile groups; therefore, synthesis of silyl derivative of polymers and copolymers could be important case in drug delivery systems. All of products were identified by spectroscopic methods. We also identified monomers by ^{1}H NMR, ^{13}C NMR, and Mass spectroscopy. A typical spectrum of ^{1}H NMR and ^{13}C NMR are shown in Figs. 1 and 2, respectively.

8.1. Identification of network polymer

The resulting network polymers swell and become soft if they are exposed to solvents such as H_2O and most organic solvents without dissolving. In the FT-IR spectra, absorption of C–Si bond appeared in the region of 1258–1270 and 837–900 cm^{-1} refer to stretching, and bending vibration, respectively, absorption in the region 1730 cm^{-1} refer to the stretching of carbonyl bond. In this way, we characterized cross-linked copolymers.

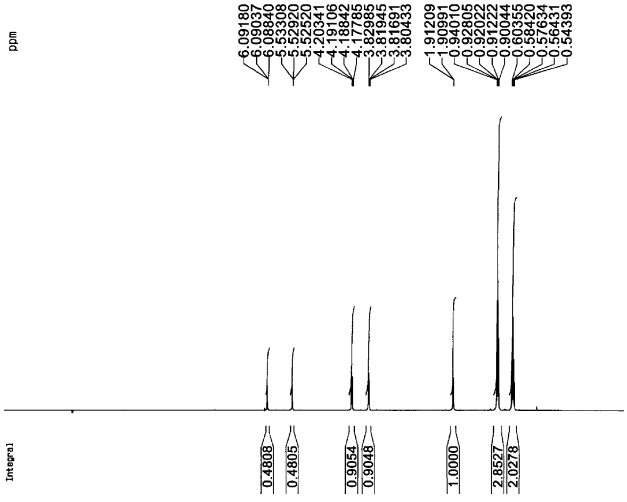


Fig. 1. ^{1}H NMR of TETMA.

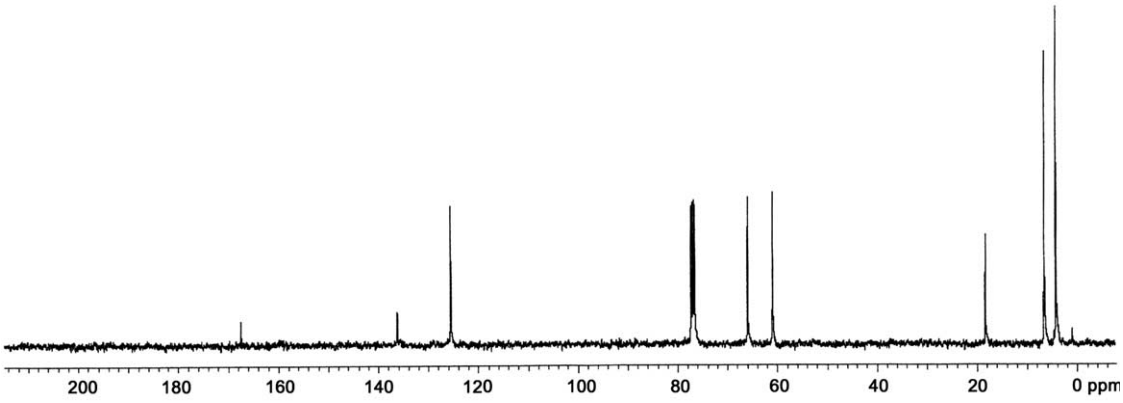


Fig. 2. ^{13}C NMR of TETMA.

8.2. Thermal behavior

Differential scanning calorimetry (DSC) was evaluated. The glass transition temperature (T_g) was determined from the DSC thermograms. The values are given in Table 1. It appears that with increasing 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 [12]. The T_g value of the homopolymer without the silyl group would be higher than T_g value of the copolymer. The silyl group as a plasticizer increases the flexibility of hard polymers and reduces its T_g. It seems that incorporation of silyl groups in side chains of polymer reduced the intermolecular interaction of chains and cause decreasing of T_g.

9. Conclusion

The copolymer and cross-linked copolymers were synthesized by free radical solution polymerization. The DSC analysis indicated that the glass transition temperature of copolymer decreases with incorporation of silyl groups in side chains of polymer. 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. Cubane-1,4-bis(methacryloyloxyethyl)carboxylate (CA) is a versatile cross-linking agent for synthesis of new cross-linking polymers for many purposes. As we said in introduction, some terpolymer of acrylate with silyl groups used as a membrane and also some other polymers such as polystyrene with silyl groups showed these properties [16], therefore, these copolymers could have membrane properties. 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. In this work, we synthesized and identified novel organosilicon monomers, and polymers of methacrylate.

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