Gamma-Rays Induced Copolymerization of Vinyl Triethoxy Silane and Methyl Methacrylate: Their Spectroscopic Characterization

TUNCER ÇAYKARA,[1] MEHMET S. EROĞLU,[2] OLGUN GÜVEN[3]

[1] Gazi University, Faculty of Art and Science, Department of Chemistry, 06500, Beşevler, Ankara, Turkey

[2] TUBITAK-Marmara Research Centre, Department of Chemistry, P.O. Box 21, 41470, Gebze, Kocaeli, Turkey

[3] Hacettepe University, Department of Chemistry, 06532, Beytepe, Ankara, Turkey

ABSTRACT: The γ-ray–induced copolymerization of vinyl triethoxy silane (VTES) with methyl methacrylate (MMA) was developed to be used in the simultaneous preservation and consolidation of archeological artifacts. A detailed analysis was performed to characterize the copolymerization reaction and conversion. The copolymers were characterized by Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance spectroscopy (NMR), gel permeation chromatography (GPC), and elemental analysis techniques. The mol fraction of VTES units in the synthesized copolymers were determined by elemental analysis of silicone pertaining to VTES segments using inductive coupling plasma spectroscopy (ICP). The effect of VTES mol fraction in the initial feed and the irradiation dose (6.5, 8.5, 10.0 kGy) on the yield of copolymerization was investigated. The yield of the copolymerization was found to decrease with increasing the VTES mol fraction in the monomer feed, and to increase with increasing the irradiation dose at each monomer composition. However, using the data obtained from the ICP measurements, the mol fraction of the VTES units in synthesized copolymers was determined to increase with increasing the VTES concentration in the initial monomer feed. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 141–147, 1999

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INTRODUCTION

For years, commercially available organofunctional silanes have been the well-known silicone-containing materials having hydrolyzable methoxy, ethoxy, or chloro moieties attached to silicone. Because they contain organic functional and silane groups in the same molecule, these materials have found extensive use in the composite field to promote bonding of fillers to polymer matrix where they serve as well-known adhesion promoters, adhesion primers, blocking agents, and coupling agents.[1–5] Despite these exceptional and diverse properties of organofunctional silanes, their formed polymers generally have low mechanical resistivity to be used directly as a polymer, and they show cold flow even at very high molecular weights, as have been in polysiloxanes. Therefore, a common way to minimize these undesirable properties and to insert a broad applicability into these materials are certainly to form their copolymer and blend systems.

One of the best-known organofunctional silane is vinyl triethoxy silan (VTES), which has three

hydrolyzable ethoxy groups attached to silicon. The hydrolysis of ethoxy groups of poly(vinyl triethoxy silane) (PVTES) gives rise to silanol (Si—OH) groups, which then condense spontaneously to form siloxane (Si—O—Si) bonds. This phenomenon causes the formation of a water-resistant polymer matrix via simultaneous inter- and intramolecular linkage, and improves the adhesive property of the copolymer-carrying VTES units against the substrates containing silicone such as stone and any hydrophilic surface. In this process bonds between the copolymers and Si-containing substrates were made by energetic interaction of formed siloxane bonds between silane groups of the substrate and organic phase. The hydrolysis reaction of the copolymer-carrying VTES and methyl methacrylate (MMA) units was previously designated.[6]

The adhesion promoter properties and chemically initiated copolymerization of the MMA with some organofunctional silanes such as γ-methacryolxy propyl trimethoxy silane (MTS) and their morphological, thermodynamic, and oxygene transport characteristics have been reported by several authors.[4,7–10] However, no detailed work has been reported yet in the peer-reviewed literature on the copolymerization of VTES with MMA, initiated with gamma radiation. In our previous work, we reported the surface free-energy properties of VTES containing copolymers of MMA.[6]

A linear copolymer carrying VTES and MMA units can be used to simultaneously preserve and consolidate the archaeological artifacts made of stone. The main role of the VTES units of the copolymer is to enhance the adhesion between the copolymer and stone or any hydrophilic surface. Here, VTES units on the copolymer chains interact favorably with Si atoms on the target surface.

The objective of this work is to report the results on the synthesis and characterization of the copolymers carrying VTES and MMA units. For this purpose, various random copolymers containing VTES units at different mol fractions were synthesized using [60]Co Gamma-radiation. The effect of the radiation dose and the mol fraction of VTES in the initial feed on the conversion and the number-average molecular weight of copolymers ($\bar{M}_n$) were also investigated.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA) was supplied by Merck. It was freed from the inhibitor by passing it through an absorption column filled with alumina (Al_2O_3). Vinyl triethoxy silane was supplied from Merck, and distilled under reduced pressure. In the distillation process, due to the moisture sensitivity of the VTES monomer, all precautions were taken to avoid its contact with air. Tetrahydrofurane (THF) and methanol were purchased from Merck. They were used as solvents and nonsolvent for copolymers, respectively. They were distilled after being dried over anhydrous calcium chloride for a day. Hydrogen fluoride (HF), used for Si determination, was purchased from Merck.

Synthesis of VTES and MMA Copolymers

To synthesize the copolymers of methyl methacrylate (MMA) with vinyl triethoxy silane (VTES) containing various VTES units, the reaction mixtures having different VTES/MMA mol ratios were placed into the glass tubes. After the reaction tubes were evacuated to 10^{-7} mmHg, the dissolved gases present in the monomer mixture were removed by freezing and thawing cycles and the tubes were flame sealed. The monomer mixture was irradiated to various doses, namely, 6.5, 8.5, and 10 kGy, with a ^{60}Co-gamma irradiator at room temperature. The dose rate was measured as 0.6 kGyh^{-1} using a standard Fricke dosimeter. After irradiation, the samples were dissolved in 5 mL THF and precipitated with 100 mL dry methanol. The precipitated samples were filtered and dried under 650 mmHg vacuum at 50°C. The conversion of monomer mixtures to copolymers was determined gravimetrically.

Determination Procedure of the Copolymer Conversion

Hydrolysis of the pendant ethoxy groups of VTES units on the copolymer chains yields silanol (Si—OH) groups that condense spontaneously and form Si—O—Si bonds. The result is intra- as well as intermolecular-linked network structure. These properties have been exploited to determine the copolymerization yield. The purified samples were hydrolyzed in the presence of water at 85°C for 24 h.[7,10] After hydrolysis was completed, the samples were kept in THF to remove the soluble part (homo-PMMA part of the samples) at room temperature for 24 h, then they were dried and weighed. The copolymerization yield values were calculated on the basis of the weight ratios of the dried sample and the weight

Table I   Copolymer Conversion at Various Irradiation Doses and VTES Concentration in Feed

Sample No	Mol Fraction of VTES in Feed	Conversion (wt %)		
		6.5 kGy	8.5 kGy	10 kGy
1	0.00	100.0	100.0	100.0
2	0.18	61.3	70.0	74.3
3	0.34	47.3	54.0	62.1
4	0.43	36.0	41.1	48.0
5	0.54	27.2	31.4	36.2
6	0.82	3.6	4.5	7.8
7	1.00	—	—	—

of the initial feed. No considerable change was observed in the weight of copolymerization products before (0.5073 g) and after the hydrolysis process (0.5038 g). This result can be considered as a proof of the incorporation of VTES and MMA units into the copolymer structure. It was previously reported that the hydrolysis of the copolymer of MMA with an another organofunctional silane, the MTS, carrying 3.22–30.6 mol % MTS units on the backbone, can completely give a polymer network.[10] Percentage yield values of the copolymerization, which was carried out at different irradiation doses and initial feed compositions, are listed in Table I. The copolymer compositions were calculated from their carbon, hydrogen and silicon content (Table II).

Instrumentation

The irradiation process of the samples was performed in a Gammacell 220 type ^{60}Co-Gamma irradiator. The FTIR spectra of thin copolymer films were collected on a Nicolet 520 spectrometer. The films were prepared by dissolving the copolymer samples in THF followed by casting on a mercury surface. The solution ^{1}H- and ^{13}C-APT (Attached Proton Test) NMR spectra of copolymers were recorded by a Bruker-AC 200L, 200-mHz NMR spectrometer. All chemical shifts were referenced to tetramethyl silane standard in CDCl$_3$. The composition of copolymers were determined by using elemental analyzer and inductive coupled plasma (ICP) spectroscope. Elemental analysis were conducted by a Carlo Erba 1106 model elemental analyzer. This analysis was based on C and H determination. For Si determination, an Atomscan 25 model ICP (U.S.A.

Table II   Elemental Analysis, ICP, and GPC Results of Copolymers Synthesized at Various Feed Monomer Concentration at 8.5 kGy Irradiation

Sample No.	Mole Fraction of VTES in Feed	Carbon (%)	Hydrogen (%)	Silicon (%)	VTES Units in Copolymer (Mol Fraction)	Empirical Formula	$\bar{M}_w \times 10^{-3}$ (g/mol)	$\bar{M}_n \times 10^{-3}$ (g/mol)	Polydispersity $(\bar{M}_w/\bar{M}_n)$
1	0.18	57.17	8.24	0.58	0.02	$C_{227}H_{390}O_{102}Si$	427	116	3.7
2	0.34	57.47	8.26	1.73	0.06	$C_{77}H_{132}O_{34}Si$	213	30	7.1
3	0.43	56.70	7.99	1.80	0.07	$C_{74}H_{124}O_{33}Si$	210	29	7.2
4	0.54	58.02	8.26	1.98	0.08	$C_{69}H_{117}O_{28}Si$	164	15	10.9
5	0.82	57.66	8.50	2.97	0.11	$C_{45}H_{80}O_{18}Si$	90	8	11.3

Thermo Jarrell Ash Argon) was used. For ICP measurements, copolymer samples were weighed and charred in an oven at 600°C for 2 h, and the remaining SiO_2 was dissolved in hydrogen fluoride. Subsequently, the HF solution was diluted to the desired volume with water, and their ICP measurements were performed. The molecular weight change of synthesized copolymers were followed by GPC using a Waters 510 HPLC pump with a Waters 410 differential refractometer and a Waters Styragel HR1 + HT6E column system, THF being the eluting solvent at 40°C. A universal calibration method was used for the determination of number-average molecular weight ($\bar{M}_n$) and weight-average molecular weight ($\bar{M}_w$) values of the copolymers. Differential scanning calorimetry (DSC) measurements of copolymers were carried out by using a Du Pont DSC-9100, with a TA-9900 data processing system under nitrogen atmosphere at a 10°C/min heating rate. DSC was calibrated with metallic indium (99.99% purity), and glass transition temperature (T_g) values of copolymers were determined at half-height of the displacement.

RESULTS AND DISCUSSION

Copolymers of methyl methacrylate, MMA, with vinyl triethoxy silane, VTES, containing various mol fraction of VTES units were prepared with gamma-rays at room temperature. The gamma-ray–initiated copolymerization of MMA with VTES is a free radicalic process, and can be designated as follows.

To observe the effect of irradiation dose and the monomer feed composition on the percentage yield of copolymerization, various MMA and VTES monomer mixtures having different mol fraction of VTES were irradiated to doses of 6.5, 8.5, and 10 kGy. It was previously reported that vinyl silanes (methoxy or ethoxy vinyl silanes) copolymerize readily with some acrylic monomers but poorly with methyl methacrylate.[10] As shown in Table I, the pure MMA (sample No. 1) completely polymerized at these irradiation doses. However, no considerable polymerization reac-

Figure 1 The change of copolymer conversion with mol fraction of VTES in feed at various irradiation doses. (●) 6.5 kGy, (▽) 8.5 kGy, (■) 10 kGy. Dose rate: 0.6 kGyh^{-1}.

tion was observed when the pure VTES sample was irradiated up to 10 kGy dose (sample No. 7). These results seem to be quite reasonable, because the reactivity ratio of MMA is higher than the reactivity ratio of VTES (reactivity ratios of MMA and VTES are 1.04 and 0.2, respectively).[12] It was observed that the copolymerization reaction of VTES with MMA is a heterogeneous reaction. As the copolymerization proceeds, the product precipitates in the monomer mixture. The data collected in Table I shows the change in conversion values of copolymerization at three different irradiation doses, with the VTES mol fraction in the monomer feed plotted in Figure 1. It is observed that when the mol fraction of VTES increases, the conversion decreases. It is interesting to note that the correlation between the mol fraction of VTES in the feed and the conversion of copolymerization is almost linear. In each VTES mol fraction the conversion increases with the dose, but the extent of this increase is not considerably high. This is most probably due to the termination by chain transfer reaction of α-carbon atoms of VTES monomer and its low reactivity ratio.[12] Moreover, the copolymers containing more than 0.15 VTES mol fraction could not be obtained. Homopolymerization of VTES has been achieved only at a relatively high dose (290 kGy). This was a viscose liquid, showed poor physical properties, and readily crosslinked via hydrolyzation when contacted with air moisture.

The results of elemental analysis and Si determination of copolymers synthesized at 8.5 kGy ir-

Figure 2   FTIR spectra of copolymer of VTES/MMA containing 0.11 mol fraction of VTES units.

radiation and their molecular weight values were collected in Table II. Copolymers having low silicon content corresponding to 1 VTES unit per 50 MMA units or highest silicon content corresponding to 1 VTES unit per 8 MMA unit could be obtained by changing the mol fraction of VTES from 0.18 to 0.82 in the initial feed. The increase in the mol fraction of VTES in the monomer feed resulted in a corresponding increase in mol fraction of VTES in the copolymer, thereby indicating the formation of random copolymers (Table II). The decrease in the mol fraction of VTES in the copolymers is the result of the reactivity ratio of VTES, which is lower than the reactivity ratio of MMA.

The $\bar{M}_n$ and $\bar{M}_w$ values of the copolymers were determined by GPC using a universal calibration method. Because the copolymers contain small amounts of VTES units, Kuhn-Mark-Houwink-Sakurada (KMHS) constants (K and a) of PMMA were employed in the universal calibration to calculate $\bar{M}_n$ and $\bar{M}_w$ values of the copolymers from the GPC data. The constants K and a were taken as 7.5×10^{-3} mL/g and 0.72, respectively. The GPC results are collected in Table II. It can be clearly seen from this table that the increase in VTES content of copolymers from 0.02 to 0.11 mol fraction causes to a considerable decrease in the $\bar{M}_n$ and $\bar{M}_w$ values of the copolymers. This is clear evidence that the termination by chain transfer

via α-carbon atoms of the VTES monomer in the copolymerization reaction is very probable.[13] However, polydispersity values increase with increasing the VTES content of the copolymers.

For the spectroscopic characterization of copolymers, IR, ^{1}H- and ^{13}C-APT NMR spectrums were recorded. The IR spectrum of copolymer containing 0.11 mol fraction of VTES units (in Table II, sample No. 5) is shown in Figure 2. In this spectrum, a strong absorption peak observed at 1735 cm^{-1} is due to C=O groups of MMA, whereas the peaks at 1080 and 486 cm^{-1} are bending and an antisymetric band of Si—O—C groups belongs to the VTES units in the copolymer chains. Moreover, the sharp absorbance peaks at 1445 cm^{-1} and 1436 cm^{-1} are due to the —CH$_2$ groups pertaining to the MMA and VTES units. The IR spectrum of copolymers provide definite evidence for the formation of copolymers.

Figure 3 exhibits a typical ^{1}H-NMR spectrum of the copolymer sample containing a 0.11 mol fraction of VTES units (in Table II, sample No. 5). We observed the peaks (δ, ppm) at $\delta = 3.8$ (due to —CH$_2$ protons of —OCH$_2$CH$_3$ of VTES), $\delta = 3.6$ (due to —OCH$_3$ protons of MMA), $\delta = 1.9$–2.1 (due to —CH$_2$ protons of MMA and VTES on the backbone), $\delta = 1.2$ (due to —CH$_3$ protons of VTES), $\delta = 1.0$–0.8 (due to —CH$_3$ protons of MMA).[11] The ^{1}H-NMR was also used to deter-

Figure 3 ^{1}H-NMR spectrum of copolymer of VTES/MMA containing 0.11 mol fraction of VTES units.

mine the structural formula of the copolymer. The ratio of the areas under the peaks of —OCH$_3$ protons of MMA (at δ = 3.6 ppm) to —OCH$_2$ protons of VTES (at δ = 3.8 ppm) was found to confirm the structure of copolymer sample (sample No. 5, in Table II).

The ^{13}C-APT spectrum of the same copolymer sample supported its proposed structure (Fig. 4).

Figure 4   ATP ^{13}C-NMR spectrum of copolymer of VTES/MMA containing 0.11 mol fraction of VTES units.

Figure 5 DSC thermograms of MMA–VTES copolymers containing various mol fraction of VTES units. (a) 0.02, (b) 0.06, (c) 0.07, (d) 0.08, (e) 0.11.

The observed peaks are (δ, ppm) at $\delta = 178.8$–178.9 (due to the carbon in the C=O of MMA), $\delta = 58.5$ (due to the carbon in the —CH$_2$ of SiOCH$_2$CH$_3$), $\delta = 54.3$ (due to the quaternary carbon of MMA), $\delta = 51.7$ (due to carbon in the —OCH$_3$ of MMA), $\delta = 44.5$ (due to the carbon in the —CH$_2$ of MMA and VTES on the backbone), $\delta = 18.7$ (due to the carbon in the —CH$_3$ of —SiOCH$_2$CH$_3$), $\delta = 16.5$ (due to the carbon in the —CH$_3$ of MMA).

In Figure 5, DSC trace of the synthesized copolymers of MMA and VTES, containing various VTES mol fractions, are given. As known, for a typical random copolymer, only one glass transition temperature between the T_gs of corresponding homopolymers can be observed (T_gs of homo-PMMA and homo-PTEVS are 120 and -62°C, respectively).[12] As shown in Figure 5, a small decrease in the T_g values of copolymers was observed with increasing the VTES content. These results are another proof for the random copolymer structure of the VTES–MMA copolymers.

CONCLUSION

A series of copolymers of VTES with MMA was synthesized in bulk using gamma radiation. The synthesized copolymers are expected to have promising applications as materials for both the preservation and consolidation of Si-containing objects. It was observed that the copolymer conversion increases with increasing the dose. With increasing of the VTES concentration in the monomer feed, the VTES content of copolymers increases as their molecular weights decrease. The ICP and DSC studies showed that these synthesized copolymers are random copolymers.

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