Preparation and Cationic Photopolymerization of Organic−Inorganic Hybrid Matrixes

James V. Crivello* and Zhibiao Mao

Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12180

Received November 19, 1996[⊗]

Surface modifications of colloidal silica by sol−gel techniques with trialkoxysilane coupling agents bearing cationically polymerizable epoxy and 1-propenyl ether groups were carried out under mild conditions. After dilution with difunctional epoxy and 1-propenyl ether monomers and the addition of an onium salt photoinitiator, the mixtures were irradiated with UV light to provide organic−inorganic hybrid matrixes. Photopolymerizations were uniformly rapid and proceeded to high conversions. Colorless, transparent, cross-linked films potentially useful as abrasion resistant coatings for plastic articles were produced.

Introduction

In many applications, the lighter weight, flexibility, formability, and resistance to breakage of transparent plastics are the chief attractive features in their use as replacements for glass. To take one example, plastic lenses have largely displaced glass lenses in eyeglasses. However, plastics have inherent drawbacks that prevent their penetration into other more demanding, high-volume applications still occupied by glass. For example, due to their poor abrasion resistance, plastics tend to scratch and haze, making them unsuited for automotive glazing. One means of circumventing this problem is to apply intrinsically hard coatings to the surface of plastic articles to improve their abrasion resistance. This approach has been widely employed, and several commercially available abrasion resistant coatings are now available for plastics.[1] Typically, these coatings are applied in solvents and then dried and cured using traditional thermal processes. More recently, abrasion resistant coatings that can be UV cured have been developed to reduce or eliminate the use of solvents which constitute a potential source of air and water pollution.[2−6] UV-cured coatings for plastics also have the added benefits that they can be applied at faster rates and consume far less energy than traditional thermally cured coatings. In addition, these materials can be applied to even thin plastics with low glass transition temperatures without causing distortion and warping usually encountered in thermal curing processes.

Currently, all commercially available UV-curable abrasion-resistant coatings for plastics are based on the photoinduced free radical polymerizations of multifunctional acrylates. However, these coatings possess certain drawbacks that diminish their attractiveness. For example, the sensitivity of free radical polymerizations to the presence of oxygen often produces a softer layer at the surface of the coating due to oxygen inhibition. Experience has also shown that these coating materials tend to have rather short shelf lives and to gel on standing. It has also proven rather difficult to stabilize these materials toward adventitious free radical polymerization. For these reasons, we decided to undertake a preliminary investigation of the possibility of developing abrasion-resistant plastic coatings based on cationic photopolymerizations. Cationic photopolymerizations have the advantage that they display no appreciable oxygen inhibition, and in addition, using this approach, one can employ a wide range of different monomer systems including epoxides, vinyl ethers, oxetanes, and many others.[7] This paper reports the results of those investigations.

Experimental Section

Materials. Colloidal silica (NALCO 1034, aqueous, 34 wt % silica, diameter 20 nm, pH = 2.8) was obtained from the Nalco Co. Amberlite IRA-904 (chloride form, 55% by weight water, 4.0 mequiv/g ion-exchange capacity), all solvents, and common chemical reagents were obtained from the Aldrich Chemical Co. and used without further purification. 2-(3,4-Epoxycyclohexyl)ethyltrimethoxysilane (**I**), (3-glycidoxypropyl)-trimethoxysilane (**III**), and trimethoxysilane were received from Hüls America. Limonene dioxide (**A**) and 3,4-epoxy-cyclohexylmethyl 3,4-epoxycyclohexanecarboxylate (CY179, **B**) were purchased, respectively, from the SCM Corp. and the Ciba Geigy Corp. 1,3-Di-2(3,4-epoxycyclohexyl)ethyl-1,1,3,3-tetramethyldisiloxane (**C**),[8] 1,1,3,3-tetramethyl-1-(2-trimethoxy-silyl)ethyl-3-(2-(3,4-epoxy)cyclohexyl)ethyl disiloxane (**II**),[9] and (4-*n*-decyloxyphenyl)phenyliodonium hexafluoroantimonate (**IOC10**)[10] were prepared as described previously. 2-(Vinyl-oxy)ethanol was received as a gift from the BASF Corporation. The preparation of 1-(1-propenoxy)-2(2-(trimethoxysilyl)ethoxy)-

---

* To whom correspondence should be addressed.

[⊗] Abstract published in *Advance ACS Abstracts,* June 1, 1997.

[1] Fischer, W.; Bobalek, E. G. *Organic Protective Coatings*; Reinhold Publishing Co.: New York, 1953. Schirman, P.; Dexter, M. *Handbook of Coatings Additives*; Calbo, L. J., Ed.; Marcel Dekker: New York, 1987.

[2] Decker, C. *J. Coat. Technol.* **1987**, *59,* 97.

[3] Hoyle, C. E. *Radiation Curing of Polymeric Materials*; ACS Symp. Ser. 417; American Chemical Society: Washington, DC, 1990; p 1.

[4] *UV Curing: Science and Technology;* Pappas, S. P., Ed.; Technology Marketing Corp.: Stamford, CT; Vol. I, 1978, Vol II, 1985.

[5] Wicks, Z. W.; Jones, F. N.; Pappas, S. P. *Organic Coatings: Science & Technology*; Wiley-Interscience: New York, 1994; Vol. II.

[6] Roffey, C. G. *Photopolymerization of Surface Coatings*; Wiley-Interscience: Chichester, England, 1982.

[7] Crivello, J. V. *Ring-Opening Polymerization*; Brunelle, D. J., Ed.; Hanser Pub.: Munich, Germany, 1993; p 157.

[8] Crivello, J. V.; Lee, J. L. *J. Polym. Sci., Polym. Chem. Ed.* **1990**, *28*, 479.

[9] Crivello, J. V.; Bi, D. *J. Polym. Sci., Polym. Chem. Ed.*, **1993**, *31*, 3121.

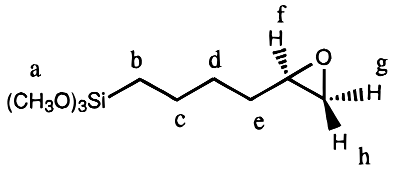
[10] Crivello, J. V.; Lee, J. L. *J. Polym. Sci., Polym. Chem. Ed.* **1989**, *27*, 3951.

S0897-4756(96)00595-9 CCC: $14.00

ethane (**V**, 36% yield, bp 0.70 °C/0.15 mmHg, 40/60 *cis/trans* mixture) is described in an accompanying paper.[11] The syntheses of 1,2-di-1-propenoxyethane (**E**, 57% yield, bp 52 °C/0.15 mmHg, 40:60 *cis/trans* mixture) and diethylene glycol di-1-propenyl ether (**F**, 69% yield, bp 62 °C/0.15 mmHg, 40:60 *cis/trans* mixture) were described previously.[12]

Synthesis of 5,6-Epoxyhexyltrimethoxysilane (IV). To a 100 mL round-bottom flask were placed 8.5 mL of 5,6-epoxy-1-hexene (0.1 mol), 1.5 equiv of trimethoxysilane (17 mL), 30 mL of toluene dried by refluxing with sodium benzophenone ketyl, and 3 mg of tris(triphenylphosphine)rhodium(I) chloride [$(PPh_3)_3RhCl$]. The resulting light purple solution was stirred and heated at 80 °C for 12 h. The solvent was removed under reduced pressure, and the resulting oil subjected to fractional vacuum distillation. 5,6-Epoxyhexyltrimethoxysilane (**IV**, bp 62 °C/0.15 mmHg) was obtained (13.5 g, 61% yield) as a colorless liquid.

^{1}H NMR ($CDCl_3$): (δppm) 3.53 (s, H_a, 9H), 0.62 (m, H_b, 2H), 3.83 (m, H_d, 2H), 1.4−1.5 (m, $H_{c,e}$, 4H), 2.83 (m, H_f, 1H), 2.69 (dd, H_g, 1H), 2.42 (dd, H_h, 1H), 5.25.



General Procedure for the Functionalization of Silica. A 50 mL round-bottom flask was fitted with a magnetic stirrer and a condenser and then charged with 5.0 g of Nalco 1034 silica, 1.0 g of a trialkoxysilane coupling agent (**I**, **II**, **III**, or **IV**), and 10 g of 2-propanol. The resulting very slightly turbid suspension was stirred and heated at 60 °C for 2 h. Amberlite IRA-904 weakly acidic ion exchange resin (100−120 mg, used as received) was added, and the suspension was stirred and heated at 60 °C for an additional 2 h. The solution was cooled to room temperature and filtered through a plug of glass wool to remove the ion-exchange resin. The resulting colorless or slightly turbid solution was combined with 4.0 g of a difunctional epoxy or difunctional 1-propenyl ether monomer and 14 g of 2-propanol. Removal of the solvent under reduced pressure yielded a colorless transparent or very slightly turbid solution or thixotropic product, which was subsequently employed in the UV polymerization studies.

Fourier Transform Real-Time Infrared Spectroscopy (RTIR). The kinetics of the cationic photopolymerization of the monomers described in this paper were followed using real-time Fourier transform infrared spectroscopic analysis (RTIR). A description of the use of this method to study the polymerization of functionallized siloxanes has been reported previously.[11] The progress of the polymerizations of the epoxy-containing organic−inorganic hybrid matrixes was determined quantitatively by monitoring the decrease of the 885 cm^{-1} band. The double bond peaks at 1660−1670 cm^{-1} were employed to monitor the polymerization of the mixtures containing 1-propenyl ether functionalized silica.

Results and Discussion

General Synthetic Approach. Abrasion-resistant plastic coatings are complex mixtures of components which are designed to interact with one another to produce a rapidly curing, hard coating. Quite early, it was found that most coatings based entirely on organic monomers did not possess sufficient hardness and abrasion resistance to provide glasslike characteristics. Instead, it was found that the incorporation of significant amounts of inorganic fillers, particularly small diameter spherical colloidal silicas, into organic coating materials greatly increases their hardness and abrasion resistance.,[13−16] Such materials are properly classified as organic−inorganic hybrid matrixes.

Accordingly, we have also incorporated colloidal silica into our approach toward the design of UV-curable coatings based on photoinitiated cationic polymerization. There are several basic problems associated with the use of colloidal silica in systems based on photoinitiated cationic polymerization. The first of these involves the complication that colloidal silicas are typically produced and supplied in water. In the course of their incorporation into a coating, these silicas must be transferred into an organic environment and the water removed. Second, the simple use of unmodified colloidal silica in organic-based coatings has not been found to give satisfactory results since these particles tend to agglomerate and to settle. Consequently, modification of the silica surfaces by attachment of organic moieties is usually required to make them more compatible with the organic components of the coating. Third, colloidal silica bears surfaces that are either strongly acidic or strongly basic. Attempts to neutralize the acidity of colloidal silica results in the immediate agglomeration of the silica particles. Further, acidic or basic colloidal silica can potentially undergo detrimental side reactions with the cationically polymerizable monomer. We have successfully overcome all of these difficulties by the application of a novel approach for the modification of colloidal silica and its use in the synthesis of photopolymerizable abrasion resistant coatings based on epoxide and 1-propenyl ether monomers.

Epoxy and 1-propenyl ether monomers undergo rapid photoinitiated cationic polymerization and can be designed to produce hard, transparent, colorless films.[17,18] Furthermore, epoxy and 1-propenyl ether monomers together with cationic photoinitiators afford shelf-stable mixtures that polymerize without oxygen inhibition effects. Accordingly, we have focused our attention in this study on the modification and incorporation of colloidal silica to make abrasion-resistant coatings based on these two types of monomers. As a starting point, it was decided to employ acidic (NALCO 1034, pH = 2.8) 20 nm colloidal silica particles and to modify them by the attachment of compatibilizing epoxide and 1-propenyl ether functional groups employing sol−gel techniques through suitable trialkoxysilane coupling agents. Similar approaches to the modification of colloidal silica and to the synthesis of hybrid organic−inorganic matrixes have been recently reported by several research groups.[16,19−24] It was anticipated that the use of basic

---

(11) Crivello, J. V.; Mao, Z. *Chem. Mater.*, previous paper in this issue.

(12) Crivello, J. V.; Jo, K. D. *J. Polym. Sci., Polym. Chem. Ed.* **1993**, *31*, 1473.

(13) Auroy, P.; Auvray, L.; Léger, L. *J. Collioid Interface Sci.* **1992**, *150*, 187.

(14) Yoshnaga, K.; Yokoyama, T.; Sugawa, Y.; Karakawa, H.; Enomoto, N.; Nishida, H.; Komatsu, M. *Polym. Bull.* **1992**, *28*, 663.

(15) Lewis, L. N.; Early, T. A.; Larsen, M.; Williams, E. A.; Grande, J. C. *Chem. Mater.* **1995**, *7*, 1369.

(16) Lewis, L.; Katsamberis, D. *J. Appl. Polym. Sci.* **1991**, *42*, 1551.

(17) Crivello, J. V. *J. Coatings Technology*, **1991**, *63 (793)*, 35.

(18) Crivello, J. V.; Löhden, G. *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34*, 2051.

(19) Bradley, R. D.; Ford, W. T.; McEnroe, F. J.; Assink, R. A. *Langmuir* **1990**, *6*, 792.

(20) Philipse, A. P.; Vrij, A. *J. Collioid Interface Sci.* **1989**, *128*, 121.

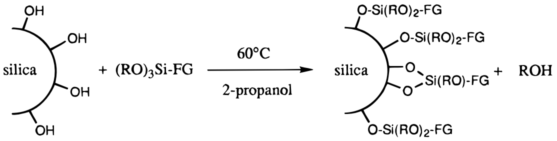
(21) Schmidt, H. *J. Non-Cryst. Solids* **1994**, *178*, 302.

(22) Wei, Y.; Wang, W.; Yeh, J.-M.; Wang, B.; Yang, D.; Murray, J. K., Jr. *Adv. Mater.* **1994**, *6*, 372.

(23) Wilkes, G. L.; Huang, H. H.; Glazer, R. H. *Adv. Chem. Ser.* **1990**, *224* (Silicon Based Polymer Science) 207.

colloidal silica, besides interacting with these functional groups, would eventually result in difficulties in inhibiting the cationic photopolymerization of the monomer-modified colloidal silica mixture.

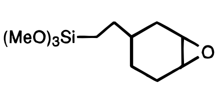
When acidic colloidal silica was combined with epoxy or 1-propenyl ether functional trialkoxysilane coupling agents at 60 °C in the presence of 2-propanol, condensation of the alkoxy groups of the coupling agent with the surface silanol moieties of the colloidal silica took place readily. Clear solutions were obtained that displayed no tendency toward aggregation. Analysis of those solutions by ^{1}H NMR showed that the epoxy and 1-propenyl ether groups of the trialkoxysilane coupling agent remained unreacted under these conditions. The reaction may be depicted schematically in eq 1 where FG is an epoxy or 1-propenyl ether functional group.



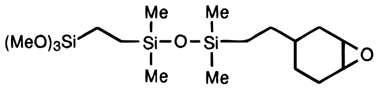
(1)

Once the sol−gel condensation was complete, the solution was diluted with a difunctional organic monomer and the 2-propanol removed under reduced pressure. The resulting mixtures were usually quite viscous, indicating strong interactions between the colloidal silica and the monomer. Normally, the products obtained according to the above-described process gelled after standing for 1−2 months at room temperature. It was assumed that the gelation mechanism involves polymerization catalyzed by the residual acidic sites on the colloidal silica. Accordingly, modified colloidal silica−2-propanol solutions were treated by stirring with an ion-exchange resin, Amberlite IRA-904, containing a small amount of adsorbed trimethylamine prior to combining them with the difunctional organic monomers. This resin is a polymeric quaternary vinylbenzylamonium chloride in the form of cross-linked beads, and for this reason it can be easily removed from the reaction mixture by simple filtration.[11] The shelf life of the resulting products after treatment with the ion-exchange resin treatment is greater than 6 months. Consequently, this stabilization procedure was performed routinely for the synthesis of the photosensitive coatings prepared during the course of this investigation.

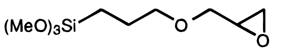
Preparation of Silica Modified with Epoxy Groups. Four epoxy functional trialkoxysilanes were employed for the sol−gel surface modification of colloidal silica. **I** and **III** are readily available from commercial sources, while the synthesis of **II** was described earlier[9] and the preparation of **IV** appears in the experimental portion of this article.



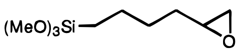
I



II

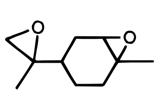


III

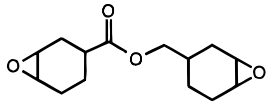


IV

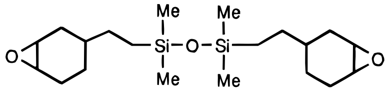
Three different epoxy monomers were combined with the corresponding epoxy functionalized colloidal silicas and their structures are shown in **A**−**C**.



A



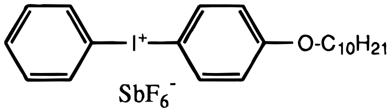
B



C

Limonene dioxide (**A**) and (3,4-epoxycyclohexyl)methyl 3′,4′-epoxycyclohexanecarboxylate (**B**) are commercially available epoxy monomers, and the synthesis of the silicon-containing epoxy monomer (**C**) was described previously[25,26] by the hydrosilation of 4-vinylcyclohexene oxide with 1,1,3,3-tetramethyldisiloxane. These monomers were selected because first they are all very highly reactive biscycloaliphatic epoxy monomers, and second all three of the monomers possess no significant UV absorption. Transparency in the UV region is desirable to maximize the rate of photopolymerization and ultimately to provide good weathering properties in the final abrasion-resistant coatings.

After removal of the solvent (2-propanol), colorless, transparent, or very slightly turbid, highly viscous products resulted. Some of the solutions displayed marked thixotropic characteristics. This suggests good interaction of the modified silica with the difunctional epoxy monomers. Under slight shearing during stirring, the initially viscous, gellike products became very fluid and could be easily spread as thin films. The photoinitiator **IOC10** (2 wt %) was readily soluble in these mixtures, and it was observed that very rapid photopolymerizations occurred on irradiation with a 200 W medium-pressure mercury arc lamp. Hard, brittle, optically transparent films were obtained in all cases after a 1−5 s irradiation.



IOC10

IOC10 was selected as the photoinitiator for these studies because it has excellent solubility in all the modified colloidal silica−monomer mixtures, good spectral response at 247 nm (ϵ = 19 500), and a high quantum yield (Φ = 0.7) and because it displays high reactivity in both the ring-opening cationic polymerizations of epoxides and the cationic vinyl polymerizations of vinyl ethers.

To more precisely follow the course of the photopolymerizations of the modified colloidal silica−monomer

---

(24) Novak, B. M. *Adv. Mater.* **1993**, *5*, 422.

(25) Crivello, J. V.; Bi, D. *J. Polym. Sci., Polym. Chem. Ed.* **1994**, *32*, 683.

(26) Crivello, J. V.; Lee, J. L. *J. Polym. Sci., Polym. Chem. Ed.* **1990**, *28*, 479.

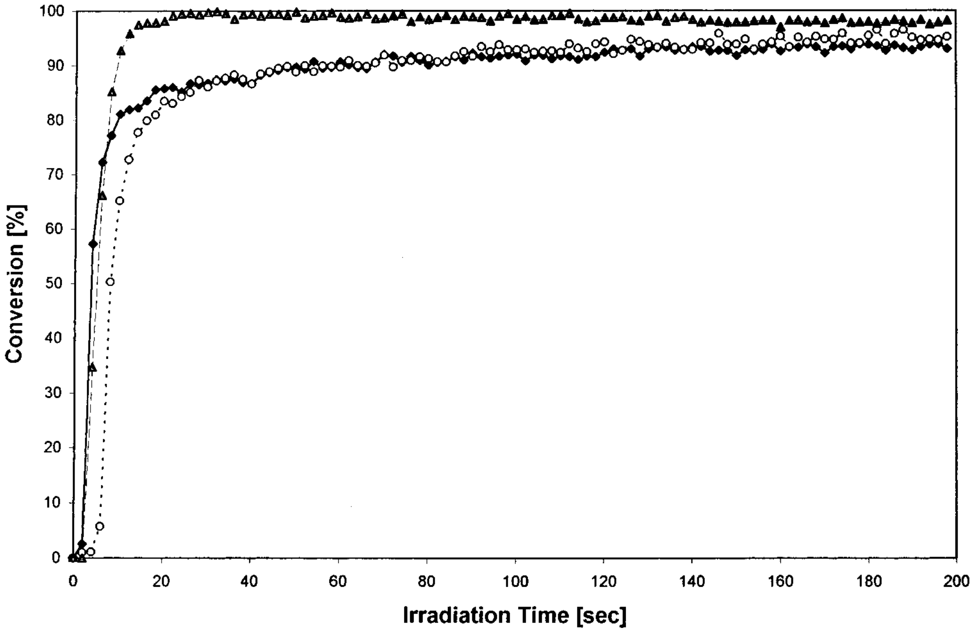


Figure 1. RTIR conversion versus irradiation time plots for the photoinitiated cationic polymerizations of (○) **I-2h-A**, (▲) **I-4h-A**, and (◆) limonene dioxide in the presence of 2% **IOC10**.

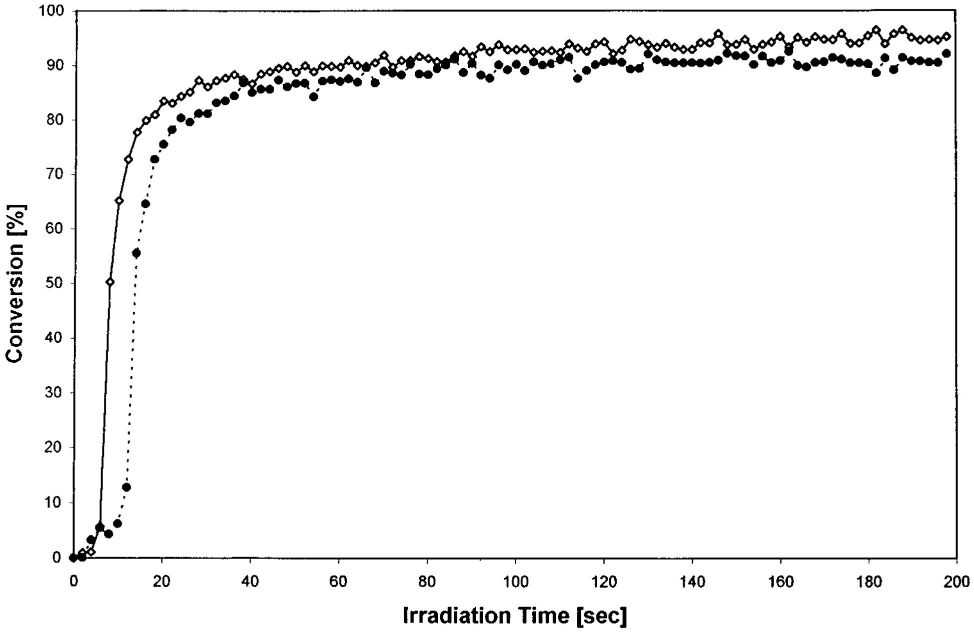


Figure 2. RTIR curves for the photoinitiated cationic polymerization of (◇) **I-2h-A** and (●) **I-2h-AT** in the presence of 2% **IOC10**.

mixtures, they were monitored using real-time infrared spectroscopy (RTIR). Previously,[27] we have described the use of this technique to monitor the polymerization of both highly reactive silicon-containing epoxides as well as other types of cationically photopolymerizable monomers. Employing this method, the decrease of the epoxide absorption at 763 cm^{-1} was followed as a function of time at low light intensities (1500 mJ cm^{-2} min^{-1}).

Figure 1 shows the conversion versus irradiation time plots of the polymerizations of the products prepared by the sol–gel modification of colloidal silica with **I** after reaction times of 2 and 4 h and after dilution with limonene dioxide (**I-2h-A** and **I-4h-A**). A corresponding polymerization curve for limonene dioxide is presented for comparison. All three samples displayed excellent, very high polymerization reactivity. This can be seen by the steep slopes of the initial portion of the conversion versus time curves. There is little difference between the curves for **I-2h-A** and **I-4h-A**, and one can conclude that a 2 h reaction period is sufficient for the modification of the colloidal silica. The mixtures containing colloidal silica gave similar ultimate epoxide conversions (95–98%) as unmodified limonene dioxide monomer.

Figure 2 shows a comparison of the RTIR curves of the photopolymerizations of **I-2h-A** before and **I-2h-AT** after treatment with the ion-exchange resin to achieve stabilization. Treatment did not effect the conversion of the polymerization, but slightly increased the induction period. This is consistent with the introduction of

---

[27] Crivello, J. V.; Jo, K. D.; Kim, W.-G.; Bratslavsky, S. A. *Macromolecular Engineering: Recent Advances*; Mishra, M., Nuyken, O., Kobayashi, S., Yagci, Y., Sar, B., Eds.; Plenum Publishers: New York, 1995; p 85.

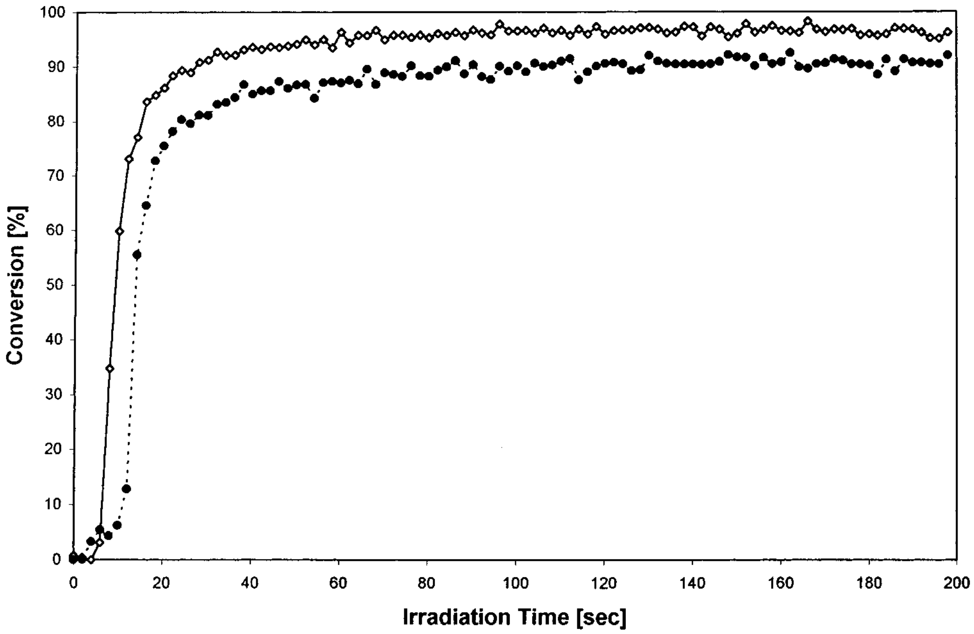


Figure 3. Comparison of the photopolymerizations of (●) **I-2h-A** (silica modified with 1.0 g of **I**) and (◇) **2I-2h-A** (silica modified with 2.0 g of **I**. Both polymerized using 2% **IOC10**.

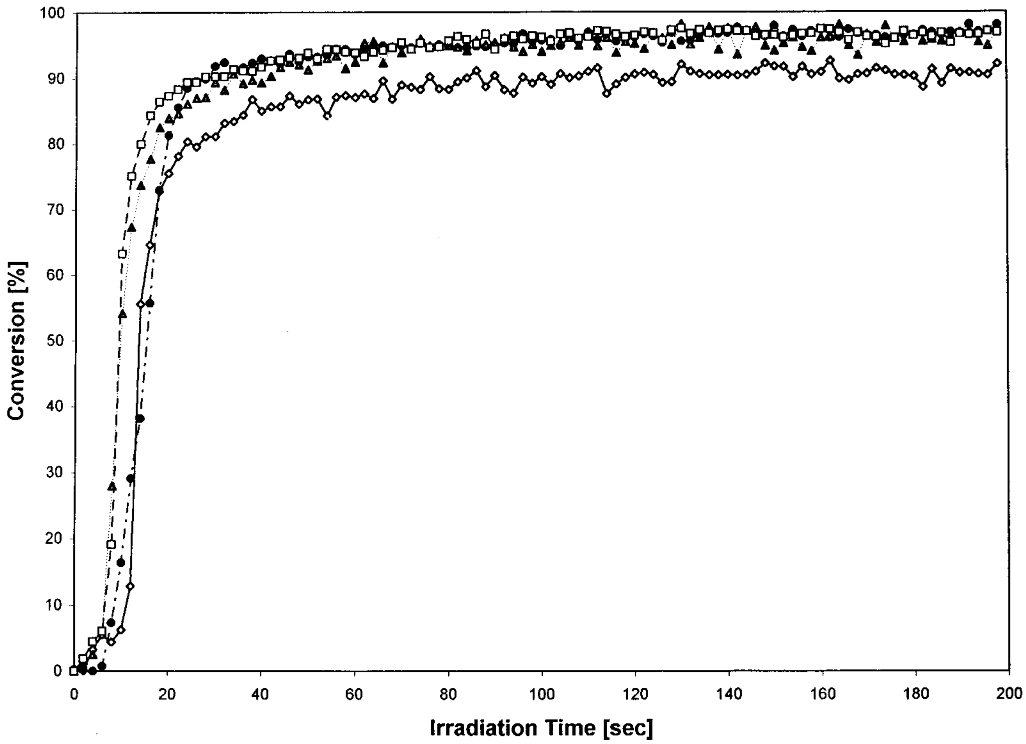


Figure 4. RTIR curves comparing the photoinitiated cationic polymerizations of (◇) **I-2h-A**, (▲) **IIA**, (●) **IIIA**, and (□) **IVA**.

a small amount of trimethylamine from the ion-exchange resin which behaves as an inhibitor of cationic polymerization. Once the induction time is overcome, polymerization takes place at the same rate as sample **I-2h-A** which was not subjected to treatment with the ion exchange resin.

The effect of variation in the amount of the trialkoxysilane coupling agent, **I**, used to modify the colloidal silica on the photopolymerization was also examined and the results are shown in Figure 3. Doubling the amount of **I** from 1.0 g in **I-2h-AT** to 2.0 g in **2I-2h-A** gave very similar polymerization conversion curves for both modified colloidal silicas.

In a similar manner, a variety of silane coupling agents [1,1,3,3-tetramethyl-1-(2-trimethoxysilyl)ethyl-3-(2-(3,4-epoxy)cyclohexyl)]ethyldisiloxane (**II**), (3-glycidoxypropyl)trimethoxysilane (**III**), and (5,6-epoxyhexyl)-trimethoxysilane (**IV**) were used to modify colloidal silica by sol−gel condensation. Combination of these materials with limonene dioxide, **A**, resulted in colorless solutions of **IIA**, **IIIA**, and **IVA**. To these solutions were added 2% **IOC10.** It was observed that the resulting mixtures polymerized readily under UV irradiation to give hard, transparent films. The results of a RTIR study comparing the photopolymerizations of these new

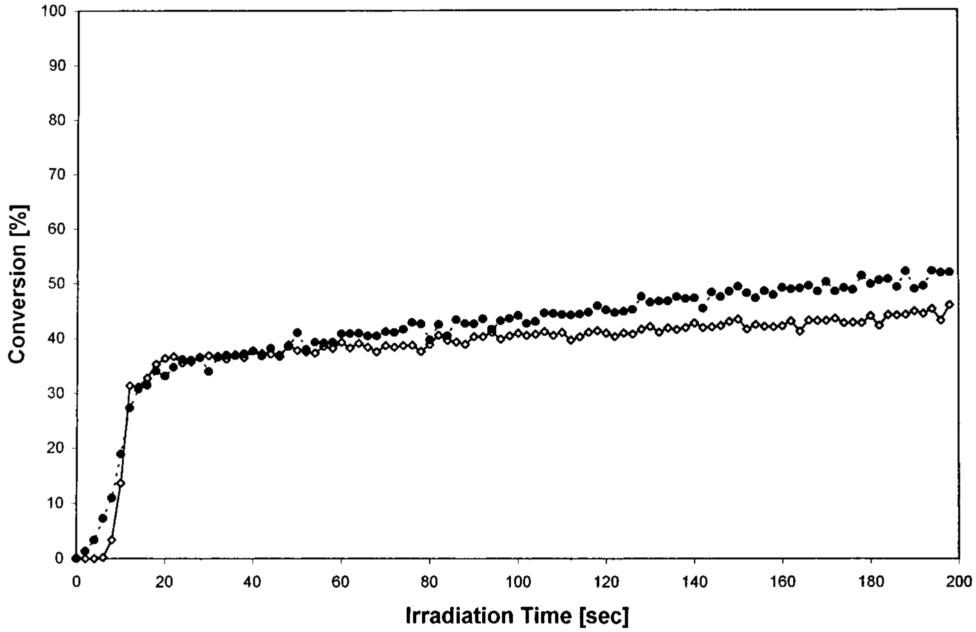


Figure 5. Comparison of the photopolymerizations of (●) **IB** and (◇) **B**.

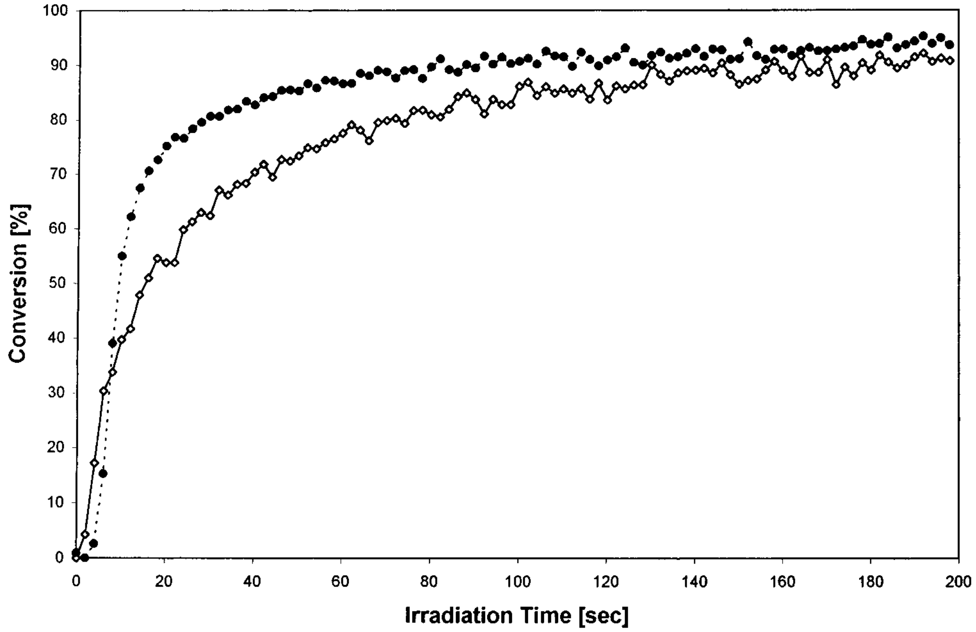


Figure 6. Comparison of the photopolymerizations of (●) **IC** and (◇) **C**.

materials are shown in Figure 4. Similar, high reactivity was observed for all these materials.

Mixtures of modified colloidal silicas with other difunctional epoxy monomers were also prepared and studied during the course of this work. Combination of modified colloidal silica **I** and the biscycloaliphatic monomers **B** and **C**, respectively, resulted in colorless, transparent or slightly turbid, thixotropic mixtures **IB** and **IC**. As before, these mixtures displayed marked shear thinning characteristics upon stirring, were good solvents for **IOC10** (2 wt %), and underwent rapid photopolymerization to give transparent films. Figures 5 and 6 respectively show the polymerizations of **IB** and **IC**, compared with those of **B** and **C**. The mixtures containing colloidal silica gave similar polymerization conversions to those of the difunctional monomers, but in both cases exhibited slightly longer induction periods. Again, we attribute this latter effect as being due to traces of tertiary amine base derived from the ion-exchange resin used to stabilize the products of the sol–gel reaction. In these latter two cases, the higher reactivity of silicon-containing monomer **C** in both the pure monomer and in the mixture with modified colloidal silica is clearly evident.

Preparation of Silica Modified with 1-Propenoxy Groups. The photoinitiated cationic polymerization of vinyl and 1-propenyl ethers has been recently investigated in this laboratory,[28–30] and the rates of polymerization of these monomers were found to be much higher than the most reactive epoxy monomers. Silicon-containing 1-propenyl ether monomers were also investigated and found to exhibit particularly high

---

(28) Crivello, J. V.; Jo, K. D. *J. Polym. Sci., Polym. Chem. Ed.* **1993**, *31*, 1483.

(29) Crivello, J. V.; Kim, W.-G. *J. Macromol. Sci.—Pure Appl. Chem.* **1994**, *A31*, 1105.

(30) Crivello, J. V.; Bratslavsky, S. A. *J. Polym. Sci., Polym. Chem. Ed.* **1994**, *32*, 2755.

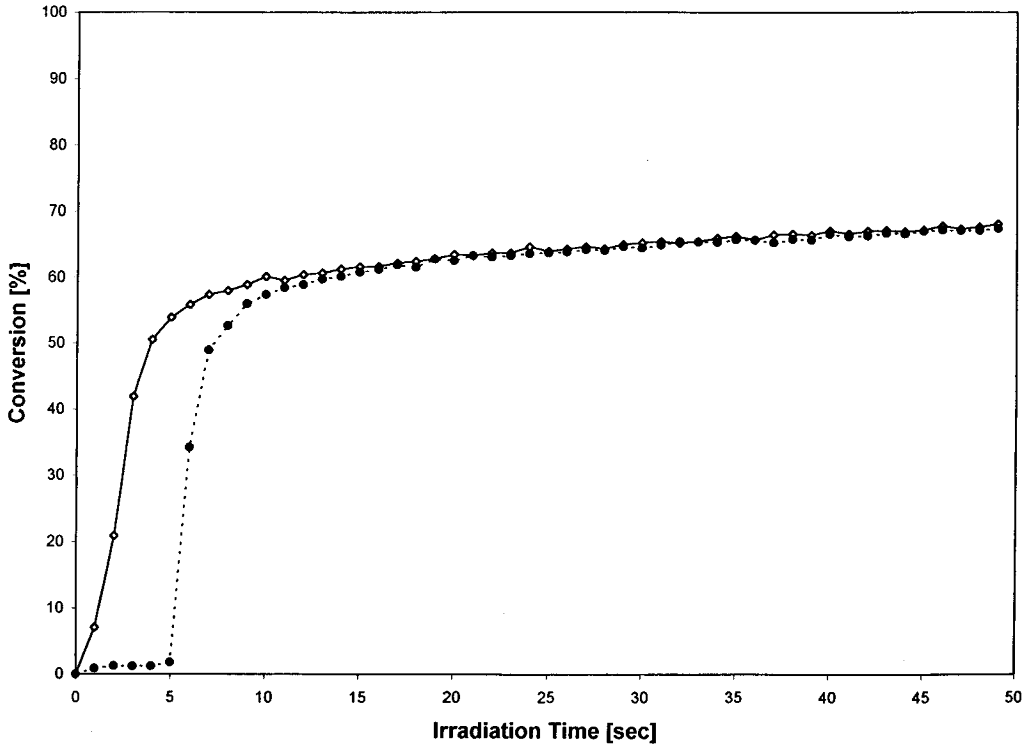


Figure 7. RTIR study of the photopolymerizations of (●) **VE** and (◇) **E**.

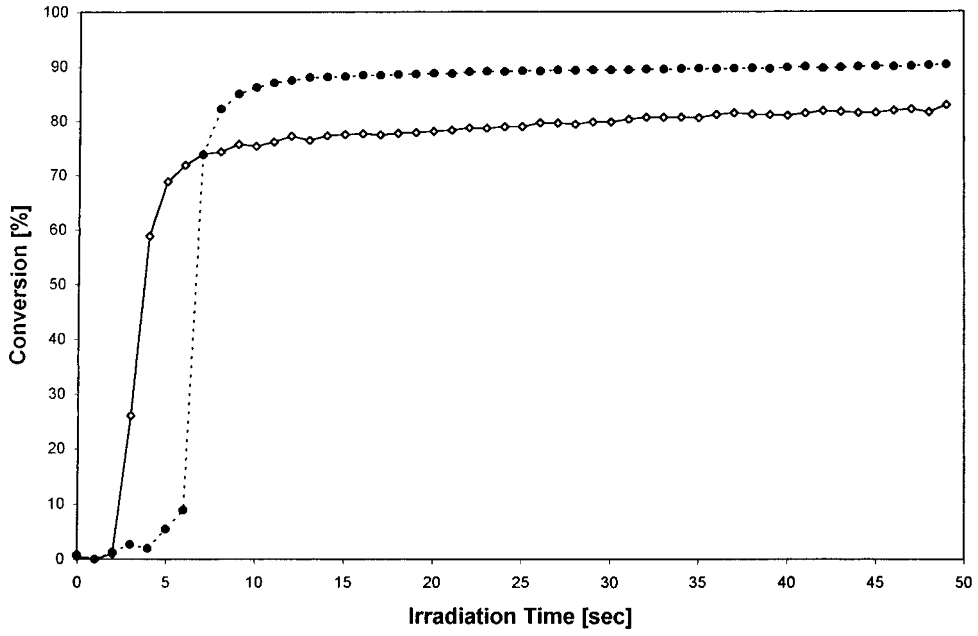


Figure 8. RTIR study of the photopolymerizations of (●) **VF** and (◇) **F**.

reactivity.[31,32] Accordingly, we undertook the synthesis of a trialkoxysilane coupling agent, **V**, fitted with a reactive 1-propenyl ether group and employed it for the modification of colloidal silica.[11] Vinyl 1-propenyl ether precursor **D** was prepared by the reaction of 2-(vinyloxy)ethanol with allyl bromide in the presence of a phase-transfer catalyst and sodium hydroxide. **D** was regioselectively hydrosilated with trimethoxysilane at the vinyl ether double bond (eq 2) to give **V**.

V was employed to functionalize colloidal silica in the same manner (60 °C, 2 h) as described for epoxy functional coupling agents **I**–**IV**. This reaction proceeded smoothly and the resulting modified colloidal silica was stabilized by treatment with the ion-exchange resin, Amberlite IRA-904, and then diluted with the difunctional monomers 1,2-dipropenoxyethane (**E**) and diethyleneglycol di-1-propenoxy ether (**F**) to give colorless solutions **VE** and **VF**. The preparation of difunctional 1-propenyl ether monomers **E** and **F** were described earlier.[12] **IOC10** photoinitiator (2%) was added, and the resulting mixtures were irradiated with a 200

$$\underset{\mathbf{D}}{CH_2{=}CH{-}O{-}CH_2{-}CH_2{-}O{-}CH{=}CH{-}CH_3} + (CH_3O)_3SiH \xrightarrow{[(C_6H_5)_3P]_3RhCl}$$

$$\underset{\mathbf{V}}{(CH_3O)_3Si{-}CH_2{-}CH_2{-}O{-}CH_2{-}CH_2{-}O{-}CH{=}CH{-}CH_3} \quad (2)$$

---

[31] Crivello, J. V.; Yang, B.; Kim, W.-G. *J. Polym. Sci., Polym. Chem. Ed.* **1995**, *33*, 2415.

[32] Crivello, J. V.; Löhden, G. *Chem. Mater.* **1996**, *8*, 209.

W medium-pressure Hg arc lamp. Less than 1 s irradiation was required to produce hard, transparent, colorless, tack-free films of these two mixtures.

Depicted in Figures 7 and 8 respectively are the RTIR curves for the photopolymerizations of mixtures **VE** and **VF**. During polymerization, the disappearance of the band at 1670 cm^{-1} due to the 1-propenoxy group was monitored. In both cases, the difunctional monomers and their mixtures with modified colloidal silica displayed excellent reactivity. The rates of photopolymerization as indicated by the initial slopes of the curves are higher for mixtures **VE** and **VF** than for their respective monomers **E** and **F**. It should be noted that both of these mixtures displayed appreciable induction periods as compared to monomers **E** and **F**. This is due to the presence of traces of amine inhibitors derived from the ion-exchange resin used to stabilize the organic−inorganic hybrid mixtures toward spontaneous gelation. Without stabilization, the mixtures gelled within a few hours. The conversions of the mixtures and their respective difunctional 1-propenyl ether monomers were similar. In Figure 7, in which the shorter di-1-propenyl ether monomer **E** was employed, the maximum conversion of 1-propenyl ether groups was 67−68%. Higher conversions were obtained as noted in Figure 8 for **VF** (90%) and **F** (83%). In this latter case, the longer chain of monomer **F** would be expected to give a cross-linked polymer with a more open network structure and corresponding lower T_g. This results in greater mobility of the functional groups within the network leading to a higher conversion.

Conclusions

Colloidal silicas functionalized with cationically polymerizable groups were prepared by sol−gel modification of colloidal silica employing trialkoxysilane coupling agents bearing epoxy and 1-propenyl ether groups. Combination of the modified colloidal silicas with a difunctional epoxide or 1-propenyl ether monomers provided mixtures which upon addition of a diaryliodonium salt photoinitiator underwent rapid cationic polymerization to give organic−inorganic hybrid matrixes when exposed to UV irradiation. Colorless, transparent films were obtained that have potential applications as abrasion resistant plastic coatings. Future communications in this area will report on the properties of the UV-curable materials and their modification for specific applications.

Acknowledgment. The authors would like to thank the General Electric Co. for their financial support of this work.

CM960595Q