Synthesis and Characterization of High Refractive Index Polythiocyanurates

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The polythiocyanurates with high molecular weights were successfully prepared by the phase-transfer catalyzed polycondensation of triazinedithiol with activated dibromides. These polymers were soluble in tetrahydrofuran (THF) and N-methyl-2-pyrrolidone (NMP), and readily afforded colorless and transparent cast films. The films of polythiocyanurates exhibited good thermal stabilities such as thermal decomposition temperatures of 320 °C in air. A relatively high glass transition temperatures of the polymers were in the range of 112-143 °C. The optical transmittance of the films was as high as 80% at 400 nm. The films exhibited high refractive index of 1.73 at d line, which is attributed to the triazine rings and sulfur atoms, and Abbe's number of around 18. Furthermore, the films showed the low birefringence of 0.0007-0.0022 at d-line. The obtained polymers are promising candidates for thermoplastic optical lens application.

Keywords: Polythiocyanurate, Triazinedithiol, High refractive index, Low birefringence, Thermoplasticity

1. Introduction
A high refractive index, low birefringence and good thermal solubility, and high optical transparency are the basic concerns in designing optical polymers for high performance components for advanced display devices, various lenses, and optical waveguides [1,2]. The advantages of polymers are their good processability, good impact resistance and lightweight compared to inorganic glasses.

Refractive indices of polymers can be expressed using the Lorentz-Lorenz equation (1) [3,4]. The equation which defines the relationship between the refractive and individual parameters depending on polymer structure is quite useful for designing high refractive index polymers.

\[
\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi \rho N_A \alpha}{3 M_W} \frac{[R]}{V_0}
\]

where \(n\) is the refractive index, \(\rho\) is the density, \(N_A\) is the Avogadro number, \(M_W\) is the molecular weight, \(\alpha\) is the linear molecular polarizability, \([R]\) is the molar refraction, and \(V_0\) is the molecular volume of the polymer repeating unit. According to the equation, the introduction of substituents with a high molar refraction and a small molar volume efficiently increases the refractive index of the polymers. Sulfur is the most commonly used atom for increasing the refractive index because of its high atomic polarizability and ability to be introduced into polymers. Various sulfur-containing polymers exhibiting high refractive index values have been synthesized and characterized for the optical applications [1,2].

Recently, in the image pickup optical system of a camera, thermoplastic lenses have been used instead of optical inorganic glasses. Several thermoplastic lenses with a high refractive index, a low birefringence have been reported such as polyesters with phenylfluorene moieties. These polymers exhibited relatively high refractive indices of 1.6 and small birefringence. Considering their use in thermoplastic lenses, their refractive indices over 1.7 are required. As well as the sulfur atom, heteroaromatic rings such as triazine [5] and pyrimidine [6] are promising components with high
refractive index due to the higher polarity of the rings, the replacement of benzene units to heteroaromatic rings might be effective for the enhancement of the refractive index.

We now report the synthesis and characterization of polythiocyanurates (III) containing sulfur atoms and triazine units prepared by the polycondensation of triazinedithiol (I) and activated dibromides (II). The polythiocyanurates exhibited excellent optical transparency as high as 80% over the wavelength of 400 nm, and furthermore afforded high refractive indices of 1.73 and low birefringence values as well as good thermal stability.

2. Experimental

2.1. Materials

2-Anilino-1,3,5-triazine-4,6-dithiol (I) supplied by Sankyo Kasei Co. was purified by recrystallization from N,N-dimethylformamide (DMF) and washed with diethyl ether. α,α'-Dibromo-p-xylene, α,α'-dibromo-m-xylene and 4,4'-bis(bromomethyl)biphenyl were used as received. Cetyltrimethylammonium bromide (CTMAB) was obtained commercially and used without further purification. Nitrobenzene was purified by distillation under reduced pressure after drying with calcium hydride.

2.2. Synthesis of polymer (IIIb)

In a flask, 0.5907 g (2.50 mmol) of 2-anilino-1,3,5-triazine-4,6-dithiol (I) dissolved in 5.1 mL of 1 M aqueous sodium hydroxide. To the solution was added 0.365 g (1.0 mmol: 40 mol%) of CTMAB. Then, to the stirred mixture was quickly added a solution of 0.6599 g (2.5 molmol) of α,α'-dibromo-p-xylene (II) in 5 mL of dry nitrobenzene. The two-phase mixture was vigorously stirred at 70 °C for 24 h under nitrogen. The reaction mixture formed an emulsion as the polymerization proceeded. The mixture was poured into 300 mL of methanol. The precipitated polymer was collected by filtration and dried at 80 °C under vacuum. The yield of the polymer was 0.677 g (80%) and the inherent viscosity was 0.93 dL/g, measured at a concentration of 0.5 g/dL in NMP at 30 °C.

IR (film): 2963-2923 (CH2), 1556 (C=N), 1510 cm⁻¹ (C=C).

1H NMR (DMSO-d6, ppm): δ 4.28 (s, 4H, CH2), 6.97-7.55 (m, 9H, Ar-H), 10.18 (s, 1H, NH).

2.3. Measurement

FT-IR spectra were recorded on a JASCO FT/IR-4200. NMR spectroscopy was performed on a Bruker AC-400P spectrometer. The molecular weights were determined using a Tosoh HLC-8220 gel permeation chromatograph with polystyrene gel column (TSK-GEL α-M) at 40 °C and eluted with NMP containing 0.01 mol/L LiBr. Thermogravimetric analysis (TG) was performed on a Hitachi TG/DTA7220 at a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) was performed on a Hitachi DSC7000 at a heating rate of 20 °C/min. The UV-vis spectra were recorded

Table 1. Synthesis of polythiocyanurates

| Polymer | Temp. (°C) | Solvent (mL) | Yield (%) | ηinhb) (dL/g) | Mn⁰/10⁴ | Mw/Mn |
|---------|-----------|--------------|-----------|---------------|---------|-------|
| IIIa    | 70        | 5            | 76        | 0.82          | 5.5     | 2.4   |
| IIIb    | 70        | 5            | 80        | 0.93          | 6.2     | 1.9   |
| IIIc    | r. t.     | 8            | 81        | 0.71          | 5.2     | 2.8   |

a) Polymerization was carried out with each monomer (2.5 mmol) in the presence of CTMAB (40 mol%) in nitrobenzene and 1 M aqueous sodium hydroxide (5.1 mL) for 24 h. b) Measured at a concentration of 0.5 g/dL in NMP at 30 °C. c) Determined by GPC on the basis of polystyrene calibration in NMP containing 0.01 mol/L LiBr.
on a Shimadzu UV-1800. The in-plane ($n_{TE}$) and out-of-plane ($n_{TM}$) refractive indices of polymer films were carried out using a Metricon Prism Coupler Model 2010/M.

3. Results and discussion

The phase-transfer catalyzed polycondensation has been preferably used for the synthesis of the polysulfides using dithiols or sodium sulfide as a nucleophilic monomer [7-9]. We had adopted this polymerization method to the synthesis of 1,3,5-triazine-containing polysulfides [5,10] by the polycondensation of triazinedithiols with α,α'-dibromoxyylene or 1,10-dibromodecane in the nitrobenzene-aqueous alkaline solution system in the presence of a phase-transfer catalyst. The synthesis of polythiocyanurates (III) from 6-anilino-1,3,5-triazine-2,4-dithiol (I) and activated dibromides (II) was investigated by the two-phase polycondensation (Scheme 1). Polycondensation was carried out in a nitrobenzene-aqueous NaOH solution in the presence of cetyltrimethylammonium bromide (CTMAB, 40 mol%) at r.t. or 70 °C for 24 h. The results are summarized in Table 1.

Three types of colorless polymers (IIIa-IIIc) with high inherent viscosities (η_{inh}) of 0.7-0.9 dL/g and number average molecular weight ($M_n$) of 52,000-62,000 were successfully obtained. The chemical structure of the polymer was characterized by 1H NMR and FT-IR spectroscopies.

The solubilities of polymers (III) are summarized in Table 2. All polymers were soluble in common organic solvents such as THF, DMF, N,N-dimethylacetamide (DMAc) and NMP, probably

Table 2. Solubility$^a$ of polythiocyanurates.

| Polymer | NMP | DMAc | DMF | THF | CHCl$_3$ |
|---------|-----|------|-----|-----|----------|
| IIIa    | +   | +    | +   | +   | -        |
| IIIb    | +   | +    | +   | +   | -        |
| IIIc    | +   | +    | +   | +   | -        |

$^a$ a) Solubility: +, soluble at room temp.; -, insoluble.

Table 3. Thermal properties of polythiocyanurates.

| Polymer | $T_g$($^a$) ($^°$C) | $T_2$($^b$) ($^°$C) | $T_1$($^c$) ($^°$C) |
|---------|---------------------|---------------------|---------------------|
| in air  | in N$_2$            | in air              | in N$_2$            |
| IIIa    | 112 319 336         | 328 343             |                     |
| IIIb    | 126 320 338         | 327 347             |                     |
| IIIc    | 143 316 338         | 327 345             |                     |

$^a$ a) By DSC at a heating rate of 20 °C/min.  b) 5% weight loss temperature by TG at a heating rate of 10 °C/min.  c) 10% weight loss temperature.

![Fig. 1. TG curves of polymer (IIIb).](image-url)

Table 4. Optical properties of polythiocyanurates.

| Polymer | $d$($^a$) (µm) | $\lambda$_{cutoff}($^b$) (nm) | Mode($^c$) | $n_{d}$($^d$) | $n_{a}$($^d$) | $n_{c}$($^d$) | $n_{ave}$($^e$) | $\theta$($^f$) |
|---------|----------------|-----------------------------|------------|--------------|--------------|--------------|----------------|-------------|
| IIIa    | 33             | 338                         | TE         | 1.7549       | 1.7329       | 1.7215       | 1.7327         | 21.9        |
|         |                |                             | TM         | 1.7539       | 1.7322       | 1.7215       | 0.0010         | 22.6        |
|         |                |                             | ($\Delta n$) | 0.0010       | 0.0007       | 0.0000       | 0.0000         |             |
| IIIb    | 25             | 336                         | TE         | 1.7543       | 1.7319       | 1.7205       | 1.7316         | 21.7        |
|         |                |                             | TM         | 1.7530       | 1.7311       | 1.7194       | 1.7316         | 21.7        |
|         |                |                             | ($\Delta n$) | 0.0013       | 0.0008       | 0.0011       | 0.0011         |             |
| IIIc    | 24             | 336                         | TE         | 1.7720       | 1.7397       | 1.7275       | 1.7389         | 16.6        |
|         |                |                             | TM         | 1.7695       | 1.7375       | 1.7252       | 1.7389         | 16.6        |
|         |                |                             | ($\Delta n$) | 0.0025       | 0.0022       | 0.0023       | 0.0023         |             |

$^a$ a) Film thickness.  b) Cutoff wavelength.  c) TE: in-plane mode, TM: out-of-plane mode.  d) Refractive index by a prism coupler: F-line, 486 nm; d-line, 589 nm; C-line, 656 nm.  e) Average refractive index at d-line: $n_{ave} = ([2n_{TE}^2 + n_{TM}^2]/3)^{1/2}$.  f) Abbe’s number: $\theta = (n_d - 1)/(n_f - n_c)$.  g) Birefringence: $\Delta n = n_{TE} - n_{TM}$. 
due to the existence of methylene units in the polymer backbone structure.

The thermal decomposition temperature and glass transition temperature ($T_g$) are quite important considering the thermal process for optical device fabrication. The thermal properties of polymers were investigated by TG and DSC measurements. The results are summarized in Fig. 1 and Table 3. Polymers (III) showed good thermal stability, a 5% weight loss temperature ($T_5$) around 320 °C under air atmosphere. The $T_g$ values of polymers (IIIa-IIIc) were in the range of 112-143 °C. Thermoplastic lenses are required to have a relatively high $T_g$ over 100 °C and high thermal decomposition temperature because injection molding is generally carried out around 100 °C higher than the $T_g$s of the polymers to increase their fluidity in the molten state. Thus, the $T_g$ of thermoplastic polymers processable by injection molding would be suitable at around 120-150 °C. Polymer (IIIc) possessed the highest $T_g$ due to the introduction of the rigid biphenylene units. m-Linkages and methylene units contributed to lower $T_g$ of polymer (IIIa).

The optical properties of the polymer (III) films with the thickness of 24-33 µm are shown in Fig. 2 and Table 4. The cutoff wavelengths ($\lambda_{cutoff}$) of the polymer (III) films were in the range of 336-338 nm, and the transmittance was as high as 80% at around 400 nm. The refractive indices ($n_d$) of the polymer (III) films were measured at d-line by a prism coupler. All the films exhibited high $n_d$ values around 1.73, resulting from the sulfur atoms and the triazine rings with a high molar refraction. The in-plane ($n_{TE}$) and out-of-plane ($n_{TM}$) refractive indices of the polymer (IIIc) film were 1.739 and 1.737 at d line, respectively by a prism coupler. The low birefringence ($\Delta n$) value of 0.002 observed for polymer (IIIc) was relatively higher than those of polymers (IIIa, IIIb) because of rigid biphenyl units. The calculated Abbe numbers for polymers (III) were in the range of 16-22.

4. Conclusion

A series of polythiocyanurates with high molecular weights were successfully prepared by the phase-transfer catalyzed polycondensation.

Fig. 2. UV-vis spectrum of polymer (IIIb) thin film.

The polythiocyanurates had a high potential as an optical material exhibiting a high refractive index of 1.73, high transparency, low birefringence, relatively high glass transition temperatures of 126-143 °C, and excellent thermal stability. Therefore, the polythiocyanurate is a promising candidate for thermoplastic optical lens application.

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Preparation and Applications of a Polysilane-allyl Methacrylate Copolymer

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Copolymers of polysilane and allyl methacrylate were prepared using the polysilane as a photoradical initiator. The polysilane block and allyl group were retained even after photopolymerization. The σ-conjugation of polysilane block in the copolymer allowed it to exhibit light absorption in the ultraviolet region. Subsequently, an ene-thiol reaction between the copolymer and mercapto-containing molecule was carried out by photocuring a thin film of the mixture. The photoreaction formed –CH–CH₂–S– bonding between the organic component and a silica component that was formed by photoysis of the polysilane block in the copolymer. Therefore, the polysilane-allyl methacrylate copolymer successfully provided a silicon-rich organic–inorganic hybrid material.

**Keywords:** Polysilane, Allyl methacrylate, Photo-polymerization, ene-thiol reaction

1. Introduction

Polysilane exhibits electron delocalization on the Si–Si main chain. These electronic states are known as σ-conjugation owing to their characteristics resembling π-conjugation in organic molecules [1]. In addition, polysilane has good electrical conductivity and light absorption in the ultraviolet region [2], which allows its application to photopolymers [3]. However, its gradual degradation in air limits its industrial applications. To develop the functionality of polysilane, polysilane-methacrylate block copolymers were synthesized using a masked disilene precursor [4]. Polysilane with a sulfide tripod terminus was synthesized to make use of the selective chemisorption of this terminus on a gold surface [5]. Our research group developed photopolymerization of methacrylate to prepare polysilane-methacrylate copolymers using the polysilane itself as a photoradical initiator to retain the polysilane block [6, 7]. In particular, we prepared a copolymer bearing an alkoxy group, which could be used to produce a polysilane–inorganic hybrid material through a sol-gel reaction with metal alkoxide [8]. However, the alkoxy group is significantly unstable for long-term storage.

To improve the weak point of alkoxy group for the sol-gel reaction, the ene-thiol reaction has

[Chemical structure image]

Fig. 1. Photo-polymerization of polysilane-allyMA copolymer.

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been applied for the fabrication of organic–inorganic hybrid materials for hard coat and negative-type resists [9, 10]. The reaction system is superior in durability, low shrinkability, flexibility, and adhesion. Therefore, replacement of sol-gel reaction with the ene-thiol reaction will allow improvements in the preparation methods and properties of polysilane–inorganic hybrid materials. Furthermore, a polysilane-containing thin film can provide a silica component through photocuring to prepare a silicon-rich organic–inorganic hybrid material, which could be used for hard coats and low dielectric materials, among others [11]. Therefore, in this study, we have prepared a copolymer of polysilane and allyl methacrylate (allylMA) using the polysilane itself as a photoradical initiator (Fig.1). Furthermore, photocuring was used to react the allyl group in the copolymer with a mercapto-containing molecule via an ene-thiol reaction to obtain a new type of organic–silica hybrid material (Fig. 2).

![Fig. 1. Reaction scheme for the preparation of a polysilane–allylMA copolymer.](image)

**Fig. 2.** Photo-reaction of polysilane-allylMA copolymer and mercapto-containing compound to fabricate an organic-silica hybrid film.

### 2. Experimental

#### 2.1 Materials

Poly(methylphenylsilane) (PMPS) was used for the photoreaction with allylMA. PMPS (product OGSOL SI-10-10) was supplied by Osaka Gas Chemicals Co., Ltd. [12]. The crude sample was reprecipitated in hexane, filtered, and dried under vacuum overnight. AllylMA was purchased from Aldrich and used after 1H-NMR analysis. Photopolymerization of methacrylate with PMPS was performed using PMPS itself as a photoradical initiator. The typical photoreaction procedure was as follows: PMPS (~ 0.5 g) and allylMA (~ 0.5 g) were dissolved in toluene (5 mL), where the molar ratio of methylphenylsilane (MPS) unit in PMPS to allylMA was determined to be approximately equimolar. The mixture was sufficiently degassed using a freeze–thaw method. After sealing the Pyrex glass tube under N₂ gas, the tube was irradiated with UV light (SEN LIGHTS CORPORATION, high-pressure Hg lamp, 10 mW cm⁻²) for 20 min. The reaction mixture was reprecipitated in hexane (300 mL) to obtain a white insoluble product. The hexane containing the insoluble product was filtered through a glass filter (pore size: 20–30 µm), and the residue was dried under vacuum overnight.

Ene-thiol reactions were performed using mercapto-containing molecules, which were purchased from Showa Denko K. K. The molecules were 1,4-bis(3-mercaptobutyloxy)butane, trimethylopropane tris(3-mercaptobutylate), pentaerythritol tetraakis(3-mercaptobutylate), and 1,3,5-tris(3-mercaptobutylxyloxyethylene)-1,3,5-triazyl. The PMPS-allylMA copolymer and mercapto-containing molecule were dissolved in THF, and the resulting solution was spin-coated on a silicon wafer. The resulting thin film was photocured under UV light and then heated to 80 °C.

#### 2.2 Measurements

The molecular weight was measured using a Shodex GPC-101 system against a polystyrene standard and in THF as the solvent. The ratio (x/y) of the number of MPS units to the number of allylMA units was determined by 1H-NMR using a JEOL JNM-ECX400 spectrometer with deuterated chloroform as the solvent. Spectroscopic measurements were recorded using a Shimadzu UV-3600 spectrophotometer, a Shimadzu IR Affinity-ATR system equipped with a zinc selenide crystal, and a Tokyo Instruments micro-Raman spectroscopy Nanofinder 30 A with 532 nm green laser. X-ray photoelectron spectroscopy (XPS) was performed using an Ulvac Phi ESCA 3057 with an X-ray tube at MgKα energy. Differential scanning calorimetry (DSC) measurements were recorded using a Seiko Instrument DSC-X5400 apparatus at a heating/cooling rate of 10 °C min⁻¹ in a temperature range of −70 to 230 °C. Molecular orbital calculations were performed using the GAMESS program with an approximation of B3LYP/6-31 G** [13].
3. Results and discussion

The product of photoreaction of PMPS and allylMA was a white powder that was soluble in toluene, THF, and chloroform. The FT-IR spectra suggested a chemical structure originating from allylMA and PMPS. For example, a peak at 1728 cm\(^{-1}\) indicated the presence of a carbonyl group of allylMA. In addition, a peak at 1470 cm\(^{-1}\) was assigned to the bending vibration of methylene in the allylMA unit of the product. The chemical shift in \(^1\)H-NMR spectrum showed that the methacryl group of allylMA reacted completely to form a single C–C bond. The details of the \(^1\)H-NMR are presented in reference [14]. A single peak observed in the GPC chromatogram confirmed the presence of only a single component in the copolymer. The reason that the allyl group was retained even after photopolymerization was a contribution to the frontier orbitals of allylMA, where the LUMO consisted of the atomic orbitals on only the methacryl group, while the HOMO had the atomic orbitals on the methacryl and allyl groups. Therefore, the HOMO accelerated the photoradical polymerization of the methacryl group with a silyl radical derived from the photoysis of polysilane.

Table 1 lists the molecular weight, content ratio \(x/y\), and UV absorption wavelength of the products. The molecular weight decreased as the photoreaction time increased, while the molecular weights of the photopolymerization products were greater than that of PMPS. Increasing photoreaction time reduced the ratio of \(x/y\). The changes in the molecular weight and \(x/y\) with increasing photoreaction time suggested that the number of MPS units decreased as the photoreaction time increased, while the number of allylMA units in the product saturated, as in our previous report [15]. As shown in Table 1, UV absorption in the range of 320–330 nm of products of 1–3 suggested the presence of a PMPS block that exhibited \(\sigma\)-conjugated characteristics even after photopolymerization. In addition, the wavelength of UV absorption became shorter as the photoreaction time increased. This suggests that the \(\sigma\)-conjugation area in the products of 1–3 tends to decrease as the number of MPS units is reduced. These results were in accordance with the \(^1\)H-NMR results, as summarized in Table 1. Furthermore, the products exhibited glass transition at 34 °C, which resulted from the allylMA block. From the above results, it was considered that PMPS was successfully connected to allylMA to form the PMPS-allylMA copolymer.

Subsequently, the copolymer was applied in an ene-thiol reaction with mercapto-containing molecules by photocuring a thin film of the mixture. We used the aforementioned four species of mercapto-containing molecules and observed very similar characteristics among the photocured thin films. Hereinafter, we will describe a result of the ene-thiol reaction using pentaearythritol tetrakis(3-mercaptopbutylate). The FT-IR results indicated that the allyl groups of the copolymer reacted completely, because the peaks at 1429 cm\(^{-1}\) assigned to C=C and 1585 cm\(^{-1}\) assigned to R–CH=CH\(_2\) were not observed after photocuring. In addition, as shown in Figure 3, the Raman spectrum of the thin film after photocuring exhibited a peak at 720 cm\(^{-1}\), which suggested that a C–S bond was formed by the ene-thiol reaction between the allyl moiety of the copolymer and thiol moiety of the mercapto-containing molecule. Although the thin film formed by photocuring was slightly sticky because of the unreacted thiol, as confirmed by the presence of a Raman peak at 2553 cm\(^{-1}\), this could be resolved by optimizing the preparation conditions for the ene-thiol reaction. Furthermore, the XPS results confirmed the formation of a

![Fig. 3. Raman spectrum of a thin film prepared from photo-reaction of polysilane-allylMA copolymer and pentaearythritol tetrakis(3-mercaptopbutylate). The solid and dotted lines indicate the Raman spectra of the copolymer and the ene-thiol product.](image-url)
silica component, as shown in Figure 4. The copolymer exhibited a peak at 101.8 eV, which was assigned to Si–Si bonding, whereas the peak at 104.4 eV of the ene-thiol reaction product suggested the formation of Si–O bonds. The thermal properties determined by DSC showed no remarkable change in heat flow up to 200 °C. This result indicates that the film exhibits heat resistance at a sufficient degree for application in hard coat and photoresist.

![Energy (eV) vs Counts](image)

Fig. 4. XPS Si2p peaks of PMPS-allylMA copolymer and the product of ene-thiol reaction with pentaerythritol tetrakis(3-mercaptoprobutyle). The solid and dotted lines indicate the XPS spectra of the copolymer and the ene-thiol product, respectively.

4. Conclusion
Photopolymerization of polysilane and allyl methacrylate was carried out using the polysilane itself as a photoradical initiator. By adjusting UV light, a polysilane-allyl methacrylate copolymer was prepared, retaining the polysilane block and allyl group. The copolymers exhibited σ-conjugation between polysilane blocks that enabled light absorption in the ultraviolet region. Furthermore, a thin film of a mixture of the copolymer and mercapto-containing molecule allowed the production of an organic–inorganic hybrid thin film. The ene-thiol reaction resulted in strong –CH–CH2–S– bonding between the organic component and silica component that was derived from the photolysis of the polysilane block in the copolymer. The results show that through photocuring, the polysilane-allyl methacrylate copolymer can provide a silicon-rich organic–inorganic hybrid material for applications such as a hard coat and low dielectric materials. Furthermore, if other species of methacrylate are inserted in the polysilane-methacrylate copolymers, new functionality can be added to the hybrid materials in the future.

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