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A Homogenous, Photocrosslinkable Poly(dimethylsiloxane-*co*-methylvinylsiloxane) Solution in an Acrylate Monomer

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In this study, a simple photocuring method is proposed for preparing PDMS elastomers using a homogenous poly(dimethylsiloxane) (PDMS) solution in *tert*-butyl acrylate (*t*BA) as an alternative way of mechanically blending two kinds of PDMS respectively containing vinyl and hydridosilyl groups over a platinum catalyst. Poly(dimethylsiloxane-*co*-methylvinylsiloxane) (PDMSc) with 30 mol% of vinyl moieties is synthesized. The functionalized PDMS is estimated to be soluble in *t*BA from theoretical calculations of solubility parameters of PDMS and several liquid monomers. The PDMS solution is satisfactorily photocured under a conventional photoinitiator. Initial modulus and strain of the photocured films increase from 144 to 552 MPa and decrease from 3.96 to 1.84, respectively, as the *t*BA content rises from 5 to 30 wt%. They are extremely transparent in a visible region ($T > 94\%$) regardless of the amount of *t*BA. The unreacted vinyl groups in PDMSc are inter- or intrareacted near 200 °C and γ-hydrogen transfer reactions from the *tert*-butyl groups in poly(*tert*-butyl acrylate) occur over 250 °C. One of the photocrosslinked films exhibits outstanding performance as an electroactive polymer in application. In essence, this study will initiate a new methodological research into provision of PDMS elastomers using an easily formulated photocrosslinkable PDMS solution.

1. Introduction

Viscous and fluid poly(dimethylsiloxane) (PDMS) is a well-known material that can be crosslinked and solidified to be elastic by mechanically mixing two kinds of PDMS respectively containing unsaturated hydrocarbon and hydridosilyl groups. The liquid-like characteristic of PDMS, although it shows high molecular weight, derives from the large Si–O–Si bond angle, the partial ionic nature and long bond length of Si–O linkage.[1,2] A hydrosilylation reaction arises between the arcrylate or vinyl and hydridosilyl groups in the PDMS main chains under a special catalyst, resulting in the network formation in PDMS followed by the change in PDMS state.[3,4] This change especially furnishes the PDMS materials with such excellent moldability that they have been utilized for molds,[5] nanoimprint stamps,[6,7] microfluidic chips,[8–10] actuators,[10–12] biomedical devices,[13,14] sensors,[15,16] E-skins,[16,17] and even for 3D inkjet printing materials.[9,18–21] But, it is difficult to produce continuously and massively the crosslinked PDMS elastomers. It is because the crosslinking reaction occurs right after mixing the each PDMS having the functional groups, resulting in rapid increase of viscosity. The long PDMS molecule chains in the blended polymers are hard to homogenously mingle within a short time. Besides, platinum, one of precious metals, is unavoidably needed as a catalyst for this reaction.

Photocrosslinking reaction of PDMS has been explored in order to overcome such the several disadvantages of the typical PDMS curing method. Especially, because the photocuring method is uninterruptedly processible, the PDMS network formation from the photocuring reaction has been employed even for 3D inkjet printing.[9,18–21] Functional groups such as vinyl, acrylate, thiol, epoxy, and amine groups have been chemically inserted in the PDMS main chains for that purpose. It is quite well known that the arcrylate groups chemically attached to PDMS main chains are reacted each other upon UV irradiation under a photoinitiator and then give rise to the PDMS networks.[9,21,22] Thiol groups can be photoreacted with unsaturated hydrocarbon groups through, so called, thiol-ene coupling.[19,20,23–25] This reaction is known to be considerably less sensitive to oxygen than established radical-based photopolymerization. A photoinitiated reaction between epoxy groups is often used for the network

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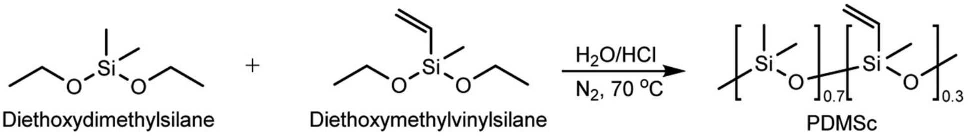


Scheme 1. Synthesis of poly(dimethylsiloxane-*co*-methylvinylsiloxane) (PDMSc).

formation.[26,27] This cationic ring-opening polymerization can occur under an ambient condition, that is, does not need an inert atmosphere, as well. This reaction rate largely depends on stability of cation intermediates and molecular structures of the epoxy groups. Even primary amine groups can be photoreacted under oxygen to give imine networks.[28,29] Singlet oxygen derived from a photosensitizer acts as an important role of the reaction.

However, the above mentioned photoactive functional groups need to be chemically added to the PDMS main chains for the photocrosslinking reaction. In addition, the use of solvents suitable for not only the PDMS, but the photoactive additives is inevitable for the homogeneous crosslinking reaction because the photoinitiator and the photosensitizer for the radical or cationic polymerization and singlet oxygen generation will not be soluble in PDMS itself. These solvents would act as a negative effect for the photocrosslinking reaction due to the chain transfer to them.[30] Furthermore, since they have to be completely removed after photocuring, we need additional equipment for the solvent evaporation and collection.

In this work, we report an efficiently photocurable and solvent-free PDMS solution. O. Okay group has recently reported some solvent-free photocrosslinkable rubber solutions in *n*-octadecyl acrylate, despite the fact that the solution homogeneity cannot be secured at high rubber concentration.[31,32] This solvent is photoreacted and crosslinked between unsaturated hydrocarbons in the rubbers, resulting in highly tough and stretchable interpenetrating polymer networks. Similarly, we have prepared a homogenous PDMS solution by using a small fraction of a liquid acrylate monomer for the first time and also tried to show possibility of using the PDMS solution for preparing PDMS elastomer materials. In order to readily prepare the functionalized PDMS, we synthesized a PDMS copolymer with lots of vinyl groups. Introduction of the vinyl moiety as many as possible into PDMS would induce the facile photocrosslinking reaction between the PDMS main chains and crosslinkers. We ultimately presented a liquid monomer that can totally dissolve PDMS and a photoinitiator. The monomer will act as not only a solvent but also a crosslinker for the functionalized PDMS. An ability of the crosslinker to dissolve PDMS was theoretically estimated from solubility parameters calculated by method Hoftyzer-Van Krevelen. Photocured PDMS elastomers were realized by using the solution. We also specifically examined physical properties of the photocured film, as compared to those of the established PDMS film, as well.

2. Result and Discussion

2.1. Preparation of Poly(dimethylsiloxane-*co*-methylvinylsiloxane) (PDMSc)

We chemically added a vinyl moiety to PDMS through condensation polymerization of diethoxydimethylsilane and diethoxymethylvinylsilane (**Scheme 1**). The copolymer was designed to have 30 mol% of the vinyl moiety. We obtained the high viscose and transparent copolymer with 62000 of number average molecular weight (Figures S1 and S2, Supporting Information). It is agreeable that the more PDMS has vinyl groups, the more easily it can be crosslinked. On the other hand, we did not add the diethoxymethylvinylsilane comonomer more than 30 mol% in consideration of degree of polymerization. In practical, when 40 mol% of diethoxymethylvinylsilane was used as a comonomer, the degree of polymerization dropped to almost one third times less than that of our PDMSc. It might be because the condensation reaction rate of hydroxyl groups in diethoxymethylvinylsilane is lower than that in diethoxydimethylsilane, even if the hydrolysis rate of ethoxide in the former is higher than that in the latter under an acidic condition.[33,34] Since, under this condition, the rate of condensation reaction is low compared to the hydrolysis rate, we need to gradually remove hydrochloric acid during the hydrolysis reaction of ethoxide groups to grow in the degree of polymerization. For that purpose, we made nitrogen flow in and out of the polymerization system at the rate of 70 mL min^{-1} and the polymerization temperature rise up to 70 °C. The ethanol and water would be eliminated during the hydrolysis and polymerization reactions, respectively. In addition, the removal of ethanol accelerates the hydrolysis reaction because the reaction is reversible. After water was found to be entirely removed, we ended this polymerization.

The several spectroscopy results (Figure S1, Supporting Information) indicate that the PDMS copolymer was found to be satisfactorily synthesized. The real composition of PDMSc was well calculated from the ^{1}H NMR spectroscopy result. The actual fractions of the two monomers incorporated into the copolymer could be determined from the peak areas at 6.0, 5.8, and 0.1 ppm assigned to $=CH_2$ and $-CH$ of the vinyl group, and $Si-CH_3$, respectively. As the mole ratio of methylvinylsiloxane moiety was revealed at about 0.29, the PDMS copolymer composition almost matched up to the feeding mole ratio. That means the vinyl groups can be quantitively included in the PDMS main chains as much as needed.

2.2. Preparations of PDMS Solutions and Photocrosslinked PDMS Films

We employed a crosslinker and a photoinitiator for efficient photocrosslinking of the PDMS containing vinyl groups, PDMSc. Though the PDMS copolymer exhibits a liquid state, it is nearly impossible to find any crosslinkers or photoinitiators soluble in the liquid polymer. Since a solvent for all elements such as a crosslinker and a photoinitiator, and even PDMS could act as a radical scavenger which is fatal to photopolymerization, we tried to find the liquid crosslinker in which both

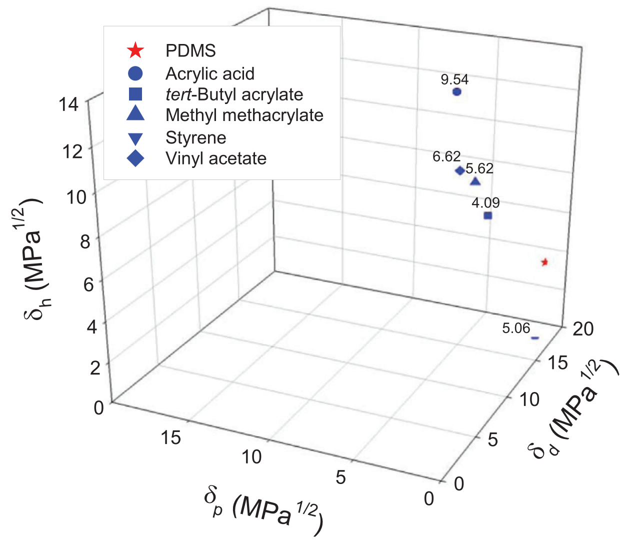


Figure 1. 3D distance ($\overline{\Delta\delta}$) of solubility parameter between each monomer and PDMS.

PDMSc and a photoinitiator can be entirely soluble. Thus, we designed a photocrosslinking system to attain a homogenous and photocurable PDMS solution by using a liquid monomer which functions as a solvent in addition to a crosslinker for the copolymer.

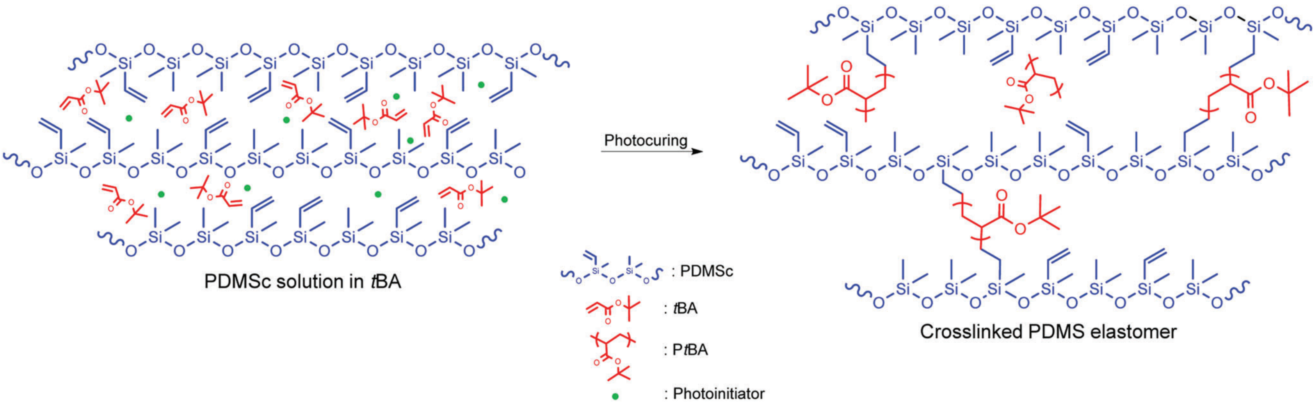
As a crosslinker, we chose several commercial and well-known liquid monomers such as acrylic acid (AA), *tert*-butyl acrylate (*t*BA), methyl methacrylate (MMA), styrene (St), and vinyl acetate (VA). First of all, as shown in Tables S1–S5 (Supporting Information), we calculated the theoretical solution parameter components (δ_d, δ_p, δ_h) contributed by dispersion, polar, and hydrogen bonding of each monomer by using method Hoftyzer-Van Krevelen.[35] Table S6 (Supporting Information) presents the experimentally provided δ_d, δ_p, δ_h values of PDMS.[36] In order to assess solubility of PDMSc in the liquid crosslinkers, 3D distance ($\overline{\Delta\delta}$) of the solubility parameter components between each monomer and PDMS was calculated by using the δ_d, δ_p, δ_h values of them and summarized in Table S7 in the Supporting Information. $\overline{\Delta\delta}$ between a solvnet and a solute must be small for good solubility. The value less than 5 is generally regarded as the good solubility on the basis of the results from the solubility of polystyrene in a number of solvents.[35,37] **Figure 1** exhibits the distance between the monomers and PDMS in a 3D space of solubility parameter components based on the results shown in Tables S1–S7 in the Supporting Information. Those distances of AA, *t*BA, MMA, St, and VA between PDMS were calculated at 9.54, 4.09, 5.62, 5.06, and 6.62, respectively. As PDMS is hydrophobic, $\overline{\Delta\delta}$ of the hydrophilic liquid monomer like AA is quite large. The distance between *t*BA and PDMS was smallest and only below than 5. Accordingly, we selected *t*BA as not only a crosslinker and but also a solvent for PDMSc. The PDMS solution in *t*BA was absolutely homogenous and the photoinitiator we used was also dissolved in *t*BA (Figure S2, Supporting Information).

When the homogenous PDMSc solution in *t*BA is exposed with UV light under nitrogen, *t*BA can be homopolymerized or be grafted and crosslinked to the PDMS main chain, as shown in **Scheme 2**. Then, the viscose PDMS solution turns to a solid. A photoinitiator also is critical for monomer activation. As a photoinitiator, we used 2,2-dimethoxy-2-phenylacetphenone with comparatively longer absorption wavelength, λ_{max} = 340 nm. The light with this wavelength can be penetrated into a glass plate, meaning that the shorter wavelength light with high energy can be considerably cut by the plate and not reach the PDMS solution layer (Table S8, Supporting Information). Additionally, the relatively long wavelength light can more deeply penetrate into the layer. The photocrosslinked PDMS film was fabricated as demonstrated in **Scheme 3**a. The film fabrication process was well explained in the experimental section. The amount of *t*BA in the PDMS solution was controlled at 5, 10, 20, and 30 wt% to investigate its concentration effect on the crosslinking reaction. All the solution layers containing *t*BA were converted to transparent films after photocuring. However, the PDMSc layer with only the photoinitiator was not solidified under the same photocuring condition. From the result, we have known that *t*BAs are crosslinked to PDMS main chains during photocuring.

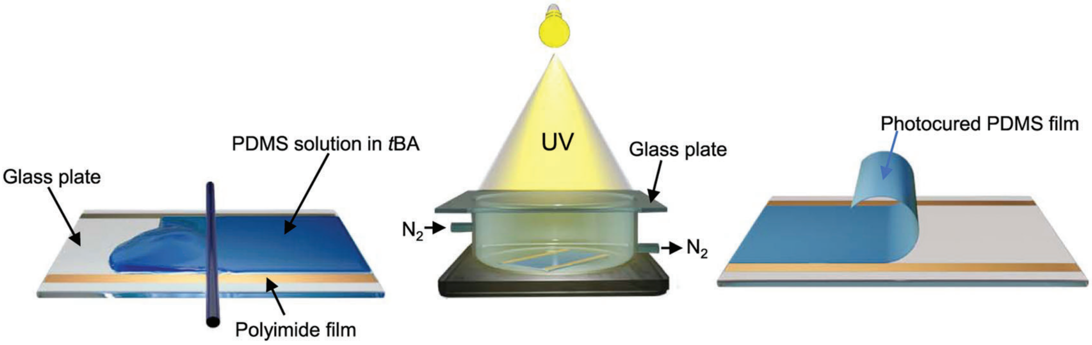
2.3. Physical Properties of the Photocured Films

We made four kinds of photocured films from the PDMS solutions with different quantity of *t*BA and examined their physical properties. The films were tremendously transparent in an entire visible region (T > 94%) irrespective of *t*BA amount in the solution, as shown in **Figure 2**a. A photograph of all the films is inset in Figure 2a. This transparency must be superior to that of the PDMS films cured from an Elastosil film.[38] The high transparency reveals that *t*BA might be mainly participated in grafting or crosslinking to PDMS main chain. Even if some *t*BAs are homopolymerized during photocuring, the domain size of poly(*tert*-butyl acrylate) (P*t*BA) is so small that the visible light is not scattered. It is because the P*t*BA particles would be molecularly distributed in the *t*BA-grafted and -crosslinked PDMS matrix.[39] Moreover, since *t*BA is a much smaller molecule than the commercial PDMS containing hydridosilyl groups acted as a crosslinker in the mechanically mixing system for curing, *t*BA is much more molecularly mixed in our photocurable PDMS solution than the PDMS crosslinker in the mixture of the Sylgard or Elastosil precursors.

In Figure 2b, we can see stress–strain curves of the photocured films, along with the pictures of the film with 5 wt% P*t*BA which were taken before and after drawing. All the films exhibited elastic properties. Since the possibility of crosslinking among the PDMS main chains rises with growing in the extent of crosslinker as well as the photocured P*t*BA is much tougher than PDMS, initial modulus (E) and maximum stress (σ) increase from 144 to 552 kPa and from 464 to 1087 kPa, respectively, as the *t*BA content in the PDMS solution escalates from 5 to 30 wt%. In this case, strain (ε) of the films decreases from 3.96 to 1.84. The initial modulus of the films fabricated from the PDMS solution containing 5 or 10 wt% of *t*BA was around 150 kPa, which approximately equates to that of the film cured from Elastosil.[40] Even though 30 wt% of *t*BA is added to PDMSc, the initial modulus and maximum stress of the film,

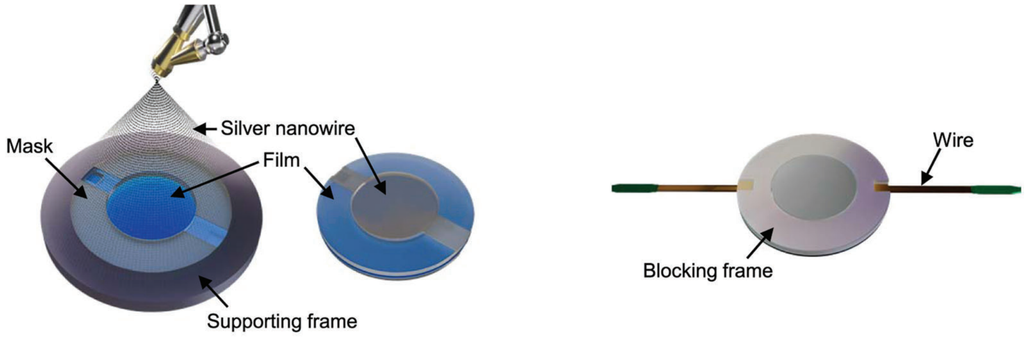


Scheme 2. Graphically represented chemical change of PDMSc solution in *t*BA during photocuring.



PDMS solution layer forming and photocuring

(a)



Flexible electrode coating and wire bonding

(b)

Scheme 3. a) Formation of a photocured PDMS film and b) fabrication of an electroactive device from the film.

552 kPa and 1.09 MPa, respectively, are lower than those of the film from Sylgard, ≈800 kPa and 4.57 MPa.[40] But, the strain between them shows almost no difference. The initial modulus and maximum stress of the photocured film can be improved by adding further *t*BA into PDMSc. The detailed results on the mechanical properties were also included in Table S9 in the Supporting Information. Thickness of the photocured PDMS films was reduced from 177 from to 134 µm as the *t*BA content expands from 5 to 30 wt% because the liquid crosslinker with low molecular weight is contracted when it is solidified during photopolymerization. The degree of crosslinking of the films also influences their swelling properties. As expected, the more *t*BA is used for dissolving PDMSc, the less swell the related photocrosslinked films (Figure 2c). Chlorobenzene is one of the good solvents for PDMS. The films were immersed in the solvent at room temperature for 72 h (inset). The volume swelling of the photocured films decreases from 404% to 88% as *t*BA content in the PDMS solution increases from 5 to 30 wt%.

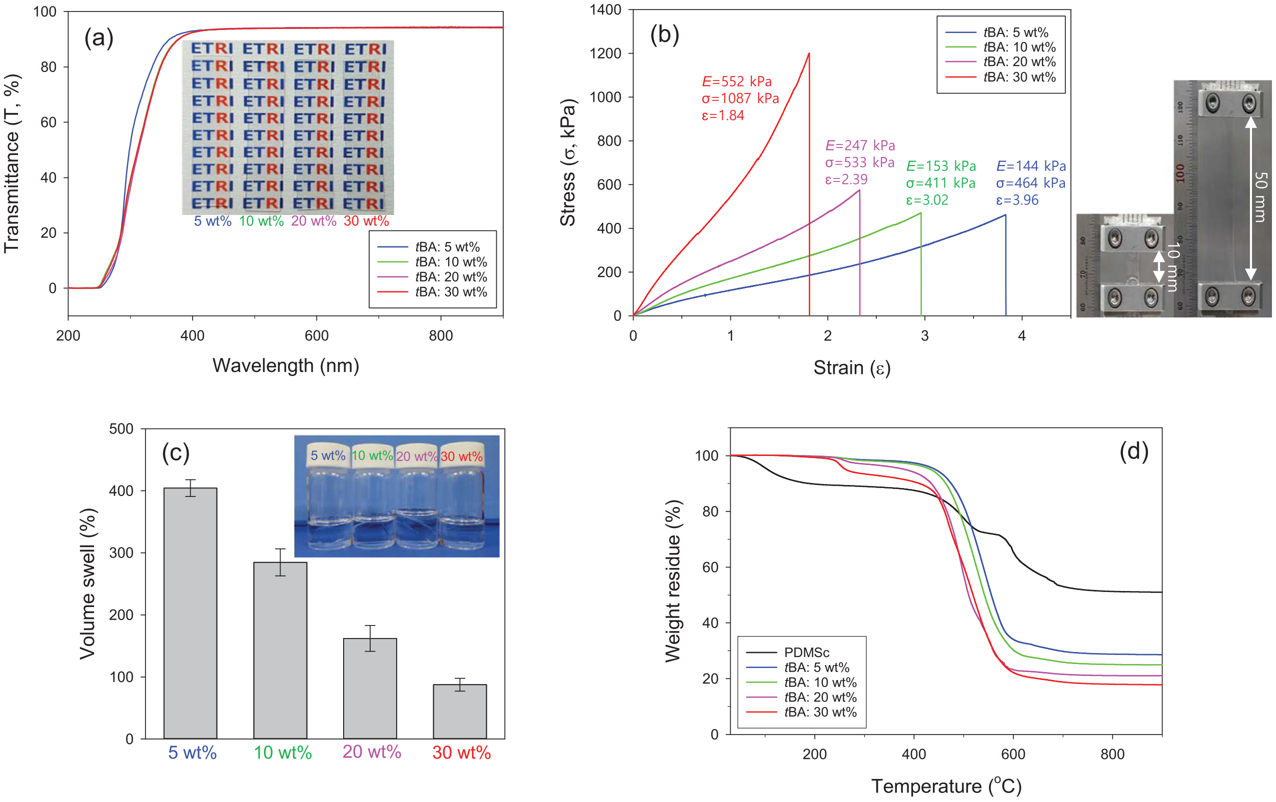


Figure 2. a) Transmittance, b) stress–strain curves, c) volume swelling in chlorobenzene, and d) thermal stability of the photocured PDMS films.

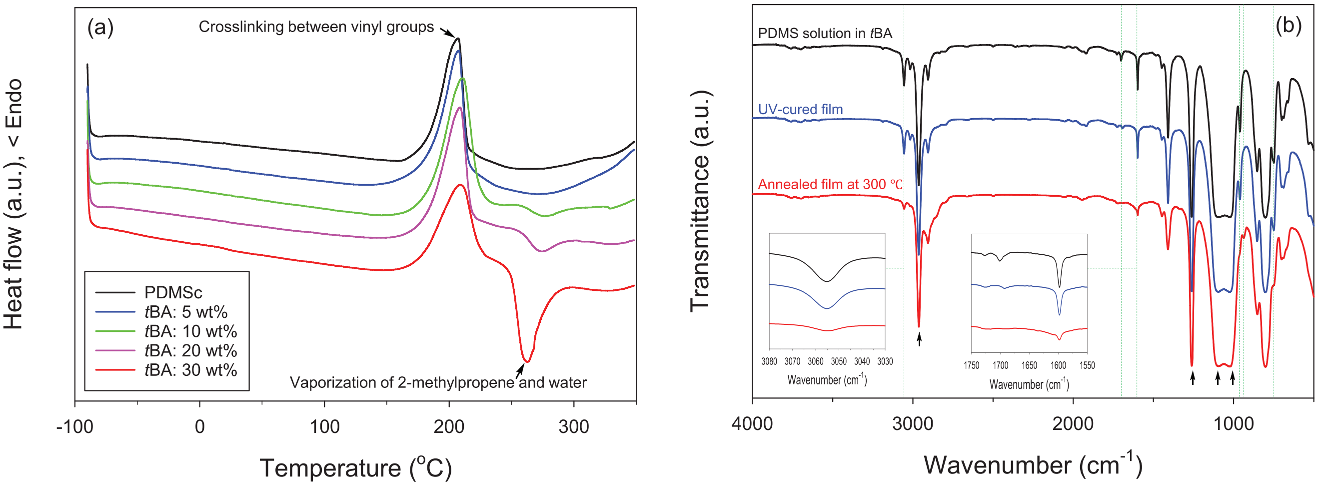


Figure 3. a) DSC results of PDMSc and the films photocured from the PDMS solutions with different amounts of *t*BA and b) IR spectroscopies of the PDMS solution with 30 wt% of *t*BA and the film annealed and photocured from the solution.

Figure 2d demonstrates thermal properties of the photocured films. First weight loss appeared near 250 °C and second one over 400 °C. The first one comes from γ-hydrogen transfer reactions from the *tert*-butyl groups to the carbonyl groups, resulting in removal of 2-methylpropene.[41,42] It is reasonable that the weight loss near 250 °C increases with the growth of P*t*BA quantity in the film. The second weight loss might be attributable to decomposition. The weight residue was 20–30% at 900 °C depending on the amount of P*t*BA. However, the weight residue of PDMSc is estimated at over 60% at 900 °C, considering the volatile things such as ethyl acetate, water, and PDMSc oligomers were thermally removed at the early heating stage.

In **Figure 3**, we can see the direct or indirect evidence of changes in chemical structures of PDMSc and the UV-cured films upon heating. Figure 3a presents changes in thermal molecular motions of PDMSc and the films photocured from the PDMS solution with different amount of *t*BA. These differential scanning calorimetry (DSC) results indicate the vinyl groups in both PDMSc and photocured films are reacted each other near 200 °C. PDMSc would be more likely crosslinked than the photocured films because the molecular motion of PDMSc is much more free than that of the photocured films. Hence, we can accept the result from Figure 2d that the thermal stability of PDMSc at high temperature appeared to be exceptionally high compared to that of the UV-cured films. Endothermic peaks also appeared between 250 and 300 °C in the photocured films containing over 10 wt% content of P*t*BA, which is owing to evaporation of 2-methylpropene or water. The evaporation phenomenon is getting more noticeable as the extent of P*t*BA in the film builds up. It is well known that the γ-hydrogens of *tert*-butyl groups in grafted, crosslinked, and/or homopolymerized P*t*BA, no matter how *t*BA was used for, are transferred to their close carbonyl groups at high temperature, producing poly(acrylic acid) (PAA) in result. The reaction product, 2-methylpropene, is eliminated as soon as it is generated during this process because its boiling point is much lower than the temperatures of γ-hydrogen transfer reaction. As soon as the carboxylic acid groups are produced in the films, they are inter or intrareacted to form anhydride groups in the PAA main chains, resulting in extra crosslinking networks and removal of water.[42,43] The expected changes in the chemical structures of P*t*BA during heating can be seen in Scheme S1 in the Supporting Information.

We can see the IR spectra differences between the PDMS solution with 30 wt% of *t*BA, its photocured and annealed film in Figure 3b. The photocrosslinked film was annealed near 300 °C for 10 min under nitrogen according to the DSC results. The absorption peaks at 3055 and 1598 cm^{-1} designated to =C–H and C=C stretching vibration, respectively, for vinyl groups of PDMSc and *t*BA or P*t*BA decrease during photocuring and annealing. The peak intensities were extensively reduced after annealing the UV-cured film, meaning the vinyl groups in the PDMS main chains are thermally reacted each other to be additionally crosslinked. The same phenomenon happened on the peak at 960 and 749 cm^{-1} related to =C–H bending vibrations. The absorption at 1701 cm^{-1} allocated to C=O stretching vibration in *t*BA or P*t*BA slightly declines during photocuring of the PDMS solution layer. This might be due to evaporation of *t*BA under our UV-curing condition. Actually, nitrogen flows into and out of the glass chamber and the inside temperature slightly rises to around 30 °C. Although this absorption peak almost disappeared after annealing as a result of the γ-hydrogen transfer from *tert*-butyl groups, any new peaks for C=O stretching vibration for the newly generated carboxylic acid groups did not appear. It is because, as shown in Figure 3a, the carboxylic acid groups vanish right after they are formed from the γ-hydrogen transfer reactions. They thermally convert into anhydride moieties by reason of inter or intrareaction between them as above mentioned. We could not find the characteristic double absorption peaks of carbonyl groups from the newly formed anhydride groups. But, another absorption peak assigned to C–O stretching vibration for the anhydride groups appeared at 937 cm^{-1}. We could see the characteristic absorption bands of PDMS at 2693, 1261, and 1096, 1023 cm^{-1}, assigned to –CH$_3$ stretching, Si–C bending, and Si–O–Si stretching vibrations, respectively.[34,40,44–46] These peak intensities are not varied during photocuring and annealing.

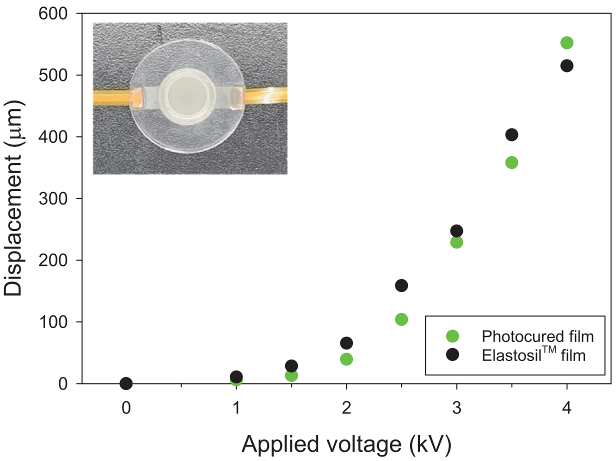


Figure 4. Electroactive performance of the photocured film with 10 wt% of P*t*BA and the Elastosil P7670 film. The image of real device fabricated from the photocured film for the measurement is inset.

2.4. Actuation Performance of a Photocured Film

We investigated electroactive behavior of the UV-cured PDMS film as an usage example of its physical properties. PDMS films have been often used as electroactive polymer (EAP) materials. Here, we fabricated a simple EAP device using the photocured PDMS film containing 10 wt% of P*t*BA as demonstrated in Scheme 3b and evaluated its electroactive performance in comparison with an Elastosil film. The device manufacturing process was described in the experimental section in detail. The evaluation result of the photocured and Elastosil P7670 PDMS films can be seen in **Figure 4**. We also catch that the displacement values and variation pattern of the photocured film with the applied voltage were roughly equal to those of the Elastosil P7670 film, respectively. We have already constructed the similar device by using the Elastosil P7670 film and simulated and appraised its electroactivity.[38] The actuation performance of the Elastosil film was akin to the behavior previously reported. The displacement means maximum variation distance of the center position of moving part before and after the voltage application. Since the film thickness lessens in case of applying voltage, the film is extended in a radial direction. This film extension is limited at the boundary between the silver nanowire coated and noncoated parts on the film, then the flat film would droop. It has been already known that the degree of decline in thickness of an EAP film is proportionate to storage permittivity and inversely proportionate to initial modulus within small deformation.[47,48] Since Figure 2b and Figure S3 (Supporting Information) reveal the initial modulus and storage permittivity values of the sample film are nearly identical to those of the Elastosil P7670 film,[40] they have been anticipated to have similar actuation efficiencies. But, in this result, our photocured film behaved a little less electroactively than the commercial PDMS film prepared by mixing the Elastosil P7670 prepolymers. That means these types of the photocured films could rival at least conventional PDMS films as an EAP material.

3. Conclusion

We have prepared an efficiently photocurable poly(dimethylsiloxane) (PDMS) solution in a liquid acrylate monomer. As chemically designed, introduction of high quantity of vinyl groups to the PDMS main chains as well as high solubility of the functionalized PDMS in the liquid crosslinker provided us a photocrosslinkable PDMS solution with high reliability. The vinyl group-containing PDMS with high molecular weight could be easily obtained from copolymerization of diethoxydimethylsilane and diethoxymethylvinylsilane. The copolymer composition could be simply controlled with the feeding mole ratio, as well. This practical manipulation of the makeup of the copolymer is advantageous to quantitively add the vinyl groups to the PDMS main chains. The calculation of 3D distances ($\overline{\Delta\delta}$) of solubility parameter between PDMS and the liquid crosslinkers was helpful for the choice of one that can entirely dissolve the functionalized PDMS among them.

We have achieved excellent photocured films from the solvent-free PDMS solution. Their physical properties were roughly identical to or even higher than those of the classic PDMS elastomers such as Sylgard and Elastosil. These films showed a superior electroactive performance. We could expect that the photocuring method for PDMS elastomer fabrication is much more convenient than the mechanically mixing method in terms of preparation of curable materials, curing time, process continuity. Moreover, our PDMS solution in *tert*-butyl acrylate can be more easily offered than other photocurable PDMS materials that many researchers have developed, considering synthesis of the functionalized PDMS and preparation of the homogeneous photocurable solution.

This study affords a new methodological research into preparation of a homogeneous, photocrosslinkable PDMS solution for PDMS elastomer fabrication. Thus, we will focus our efforts on examining the other PDMS-dissolving liquid monomers or prepolymers and their effects on physical properties of the photocured elastomers in future.

4. Experimental Section

Materials: Acrylic acid, *tert*-butyl acrylate, methyl methacrylate, styrene, vinyl acetate, chlorobenzene, chloroform-d_1, 37% hydrochloric acid solution in water, and 2,2-dimethoxy-2-phenylacetophenone were obtained from Aldrich Chemical Co., Inc. Diethoxydimethylsilane and diethoxymethylvinylsilane were acquired from Tokyo Chemical Industry Co., Ltd. Ethyl acetate and anhydrous magnesium sulfate were purchased from Junsei Chemical Co., Ltd. All chemicals were used without purification.

Synthesis of PDMSc: 21.78 g of diethoxydimethylsilane, 47.01 g of diethoxymethylvinylsilane, and 7.0 mL of distilled water were put into 250 mL of 3-necked round flask. After cooling the solution, 1.8 mL of 37% hydrochloric acid was dropwise added into it with stirring at the rate of 250 rpm min^{-1}. Nitrogen was flowed into the flask at the rate of 70 mL min^{-1}. The reaction temperature was escalated to 70 °C. The reaction was completed right after the water was completely removed in this flask. 150 mL of Ethyl acetate (EA) was added to the viscose polymer for dilution. 700 mL of distilled water was poured into the homogenous polymer solution in EA to get rid of the hydrochloric acid. The polymer solution was dried with anhydrous magnesium sulfate. Then, EA was eliminated from the solution by using a vacuum evaporator after the magnesium sulfate was filtered off. The transparent, colorless, and viscous polymer was dried at 40 °C under vacuum for 2 d (Yield: 30.9 g, 88%); ^{1}H NMR (500 MHz, CDCl$_3$, δ): 5.91–6.04 (m, 2H, –CH=CH$_2$), 5.78–5.82 (m, H, –CH=CH$_2$), 0.08–0.19 (m, 9H, –CH$_3$); ^{13}C NMR (500 MHz, CDCl$_3$, δ): 135.91–136.09 (m, –CH=), 131.69–131.82 (m, =CH$_2$), 0.00–0.03 (m, –CH$_3$); IR (NaCl, ν, cm^{-1}): 3055m (=C–H str., –CH=CH$_2$), 2963s, 2905m (C–H str., –CH$_3$), 1598m (C=C str., –CH=CH$_2$), 1408m (C–H ben., –CH$_3$), 1093s, 1023s (Si–O–Si str.); GPC (THF, polystyrene standard): M_n = 62490; M_w = 129746.

Estimation of 3D Distances ($\overline{\Delta\delta}$) of Solubility Parameter between Liquid Crosslinkers and PDMSc: First, the solution parameter components (δ_d, δ_p, δ_h) contributed by dispersion, polar, and hydrogen bonding of each crosslinker can be calculated from its group contributions using the Equation (1)

$$\delta_d = \frac{\sum F_{di}}{V},\ \delta_p = \frac{\sqrt{\sum F_{pi}^2}}{V},\ \delta_h = \sqrt{\frac{\sum E_{hi}}{V}} \tag{1}$$

where F_{di} and F_{pi} are a molar attraction constant contributed by dispersion and polar components, respectively. E_{hi} and V are hydrogen bonding energy and a molar volume, respectively.

The values of δ_d, δ_p, δ_h of PDMSc are substituted by the experimental ones of PDMS. The solubility parameter of the liquid crosslinkers was evaluated by using the Equation (2)

$$\delta = \sqrt{\delta_d^2 + \delta_p^2 + \delta_h^2} \tag{2}$$

$\overline{\Delta\delta}$ between the crosslinker and PDMSc can be calculated using the Equation (3)

$$\overline{\Delta\delta} = \sqrt{(\delta_{d,p} - \delta_{d,s})^2 + (\delta_{p,p} - \delta_{p,s})^2 + (\delta_{h,p} - \delta_{h,s})^2} \tag{3}$$

where $\delta_{d,p}$, $\delta_{p,p}$, $\delta_{h,p}$ and $\delta_{d,s}$, $\delta_{p,s}$, $\delta_{h,s}$ are δ_d, δ_p, and δ_h of a polymer and a crosslinker, respectively.

Preparation of a Photocured PDMS Film: PDMSc and 2, 2-dimethoxy-2-phenylacetophenone were fully dissolved in *t*BA. The concentration of photoinitiator was 0.5 mol% with respect to total vinyl and acrylate groups in PDMSc and *t*BA. The concentration of *t*BA was fixed at 5, 10, 20, 30 wt%. The detailed extent of ingredients is summarized in Table S10 in the Supporting Information. The PDMS solution layer was cast by a Doctor-knife method after the homogenous polymer solution was poured onto a glass plate. Thickness of a polyimide spacer was ≈300 µm. The glass plate put into a closed glass container where nitrogen flowed through and the layer was exposed to UV light for 10 min. The colorless, transparent photocured film was dried under vacuum at 60 °C for 4 h in order to remove unreacted *t*BA. In order to identify the *t*BA role in the photocuring reaction, a PDMSc solution in EA was formulated. EA was used as a solvent instead of *t*BA and the concentration was 10 wt%. Other experimental conditions were same above.

Swelling Test of Photocured Films: The dried films which weigh 50–60 mg were immersed in chlorobenzene (1 mL/20 mg) at room temperature for 72 h. The area of the sample films was ≈300 mm^2. The solvent on a surface of the swollen films was totally eliminated by washing shortly with EA and blotting them with a dry filter paper twice. Then, the films were weighed. The swollen volume fraction (υ) of the films is given by the Equation (4)[49–52]

$$\upsilon = \frac{(W_1 - W_0)\,\rho_p}{W_0 \rho_s} \times 100 \tag{4}$$

where W_0 and W_1 are the sample weight before and after swelling, respectively. ρ_p and ρ_s are the density of PDMS (1.1 g mL^{-1}) and chlorobenzene (1.106 g mL^{-1}), respectively. The density of P*t*BA is known as about 1.08 g mL^{-1}. Since the amount of PDMS is much larger than that of P*t*BA in the photocrosslinked films, the density value of PDMS was applied to calculate their volume swelling.

Fabrication of an Electroactive Polymer (EAP) Device: Scheme 3b explains the fabrication process of an EAP device in detail. After photocured film containing 10 wt% *t*BA was hold up and down with a supporting frame, 3 × 10^{-3} wt% silver nanowire suspension in isopropyl alcohol was spread onto the film except for the hidden part below a mask. After removal of the mask and supporting frame, a blocking frame was tightly put on the both sides of the nanowire-noncoated part to fix the edge of moving part. The diameter of the movable part is 12 mm. Then, the wire was bonded to the nanowire electrode.

Measurements: Infrared (IR) spectra were obtained from a Nicolet 6700 FT-IR spectrometer. The PDMS copolymer and the PDMS solution in *t*BA were thinly spread on NaCl window for the IR measurement. The coated PDMS solution layer was also photocured and annealed under nitrogen for 10 min. UV–vis spectra of the photocured films were recorded by using a Shimadzu UV-2600 spectrometer. After PDMSc was dissolved in $CDCl_3$, ^{1}H and ^{13}C NMR spectroscopy results of the PDMS copolymer were attained using a Bruker 500 MHz NMR spectrometer. The molecular weight of PDMSc was estimated using a Waters 2690 Alliance gel permeation chromatograph (GPC). Thermal analyses of the photocured films were acquired by using a TA DSC 250 differential scanning calorimeter and a TA TGA 55 thermogravimetry analyzer under nitrogen. The heating rate was 10 °C min^{-1}. TA Instrument RSA-G2 and Agilent E4890A Precision LCR meter were used for evaluations of mechanical and electrical properties of the films. The film was cut into 5 mm wide strips and the initial length for the tensile test was 10 mm. The gold electrode with 25 mm diameter and 50 nm thickness was formed on both side of the film surface by a vacuum-evaporation method. High voltage was applied to the EAP device by using a Matsusada AMT-10B10-L(230 V) high voltage amplifier and a Keysight 33210A function generator. Deformation of the photocured film was determined with a Polytec PSV-500 scanning vibrometer. The intensity of UV arriving at the surface of polymer solution layer was measured with an UV Power Puck II radiometer.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

acrylate monomers, photocrosslinkable solutions, photocured elastomers, poly(dimethylsiloxane) copolymers, solubility parameters

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