

# Effect of Copolymerizing Fluorine-Bearing Monomers on the Relationship among Internal Structure, Gas Permeability, and Transparency in Copolymer Networks Composed of Methacrylates and Siloxane Macromers

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**ABSTRACT:** To clarify the effect of the type of acrylic monomer and the molecular weight ( $M_n$ ) of polydimethylsiloxane (PDMS) on the relationship among the internal structure, oxygen permeability coefficient [ $P(O_2)$ ] and transparency, crosslinked copolymers were prepared with two different acrylic monomers: methyl methacrylate (MMA) and trifluoroethyl methacrylate (TFEMA). PDMS macromers with  $M_n$  of 1700, 3300, 4700, and 7800 g/mol were used. DSC measurements suggested that all constituent phases were insoluble with each other. The  $M_n$  of PDMS affected both the light transmittance and  $P(O_2)$ . The relationship between the  $M_n$  and  $P(O_2)$  over the low  $M_n$  range (1700 and 3300 g/mol), and the calculated PDMS domain size ratio, were found to support the  $[M_n]^{2/3}$  rule into the crosslinked copolymer. Furthermore, a 3300 g/mol  $M_n$  copolymer became transparent when the amount of PDMS was greater than PMMA. In addition, copolymerization with TFEMA drastically affected those properties, and this effect was much greater than the effect of the PDMS  $M_n$ . To clarify the mechanism of  $P(O_2)$  improvement induced by TFEMA copolymerization, calculations on the relationship among the  $P(O_2)$ , PDMS volume fraction, and morphology model were performed, and some properties such as solubility parameters should play important roles. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** siloxane macromer; oxygen permeability coefficient; morphology; transparency; fluoroalkyl group bearing vinyl monomer

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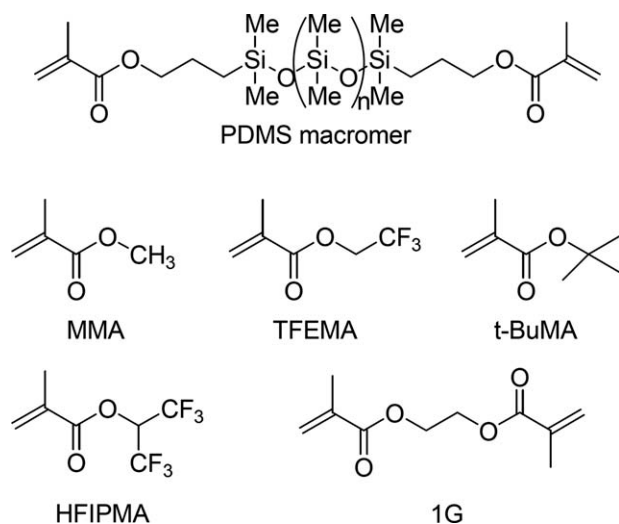
## INTRODUCTION

Silicone compounds<sup>1–9</sup> possess superior characteristics in terms of gas permeability and have been used for medical applications such as contact lenses. However, short Si—O—Si chains bearing silicone monomers lead to various undesired properties, such as the fragility and hydrophobicity due to their weak intermolecular forces and strong hydrophobicity. To overcome these issues, the introduction of silicone compounds having long Si—O—Si chains such as polydimethylsiloxane (PDMS) into the polymer backbone have been developed. Polycondensation was one approach for the introduction of a PDMS chain with a rigid segment, such as polyamide and polyimide groups, as multi-block copolymers.<sup>10–13</sup> The resultant copolymer had improved mechanical strength and solubility, but the polycondensation

approach limited the monomer type and composition ratio, based on the esterification and amidation.

Another approach is the radical copolymerization with an acrylic monomer and a PDMS macromer bearing vinyl groups at the PDMS chain ends. This approach enables the usage of a variety of characteristics of the acrylic monomers. Moreover, the composition ratio between the PDMS and acrylic monomers can be controlled by the feed conditions, and this allows a systematic study on the relationship between the physical properties and the copolymer composition, which is important for medical applications. However, there are very few articles describing the aforementioned crosslinked copolymers<sup>14,15</sup> and no reports were found on the relationship among the transparency, oxygen permeability, internal structure, and the type of acrylic monomers.

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**Figure 1.** Chemical structures of the monomers and crosslinker.

In this study, we prepared crosslinked copolymers composed of PDMS macromers and acrylic monomers at varied composition ratios by the radical polymerization method, to examine the effects of the composition on the physical properties. We selected trifluoroethyl methacrylate (TFEMA), which possesses a low refractive index comparable with silicone compounds, and methyl methacrylate (MMA), which is used as an optical material and has a relatively high  $T_g$ .

## EXPERIMENTAL

### Materials

PDMS macromer was purchased from Shin-Etsu Chemical and was used without further purification. Molecular weight ( $M_n$ ) measurements by  $^1\text{H-NMR}$  were performed with a JEOL ECS400 spectrometer using  $\text{CDCl}_3$  as the solvent, and the GPC measurements were performed with a HLC-8120 GPC system by the TOSOH Corporation (Japan). MMA (Wako Pure Chemical Industries), TFEMA (Osaka Organic Chemical Industry), *tert*-butylmethacrylate (*t*-BuMA, Wako Pure Chemical Industries), hexafluoroisopropylmethacrylate (HFIPMA, Synquest Labs), ethyleneglycoldimethacrylate (1 G, Shin-Nakamura Chemical), 2,2'-azobis (2,4-dimethyl-valeronitrile) (V-65), and 1,1'-azobis (cyclohexane-1-carbonitrile) (V-40) (both from Wako) were used without further purification. The chemical structures of the monomers and crosslinker are shown in Figure 1.

### Preparation of the Crosslinked Copolymer from Acrylic Monomer and PDMS Macromer

The preparation of the crosslinked copolymer was performed by bulk polymerization in a sheet shape. PDMS macromers with four different  $M_n$  values, MMA, TFEMA, *t*-BuMA, and HFIPMA as methacrylates, 1 G as the crosslinker (added at 1 wt % of the methacrylates) plus V-65 and V40 as the initiators, were combined according to the required balance and degassed by five repeated freeze-thaw cycles under nitrogen. The mixtures were injected between a glass plate and a polytetrafluoroethylene film separated with a silicone elastomer gasket (0.2–0.5

mm thickness) under a nitrogen atmosphere. The polymerization was then performed by keeping the temperature at  $50^\circ\text{C}$  for 16 h, followed by elevating the temperature to  $110^\circ\text{C}$  using steps of  $20^\circ\text{C}$  and 2 h. After polymerization, the polytetrafluoroethylene film and silicone gasket were removed, and then the crosslinked copolymer sheet was removed from the glass plate. For the annealing of the copolymers, obtained crosslinked copolymer sheets were kept at  $115^\circ\text{C}$  for 16 h *in vacuo*. The properties of the crosslinked copolymer were evaluated after annealing. The attenuated total reflection (ATR) FTIR spectra of some samples were recorded to monitor the residual methacryloyl groups.

### Evaluation of Crosslinked Copolymers

Light transmittance was measured by a SM-5 color computer (Suga Test Instruments). The  $P(\text{O}_2)$  was measured with a GTR-10XACT gas transmissibility measurement apparatus (GTR Tec corporation) at  $35^\circ\text{C}$ . The  $T_g$  was measured by a SEIKO Instruments Exstar 6000. The Vickers hardness was measured with an AKASHI hardness tester MVK-G1.

## RESULTS AND DISCUSSION

### Molecular Weight of PDMS Macromers

The molecular weights from the manufacturer and the results from the  $^1\text{H-NMR}$  and GPC measurements of the PDMS macromer are shown in Table I. As the results from the  $^1\text{H-NMR}$  and GPC measurements showed similar values as those from the manufacturer, the  $M_n$  from the manufacturer was used in the following analysis.

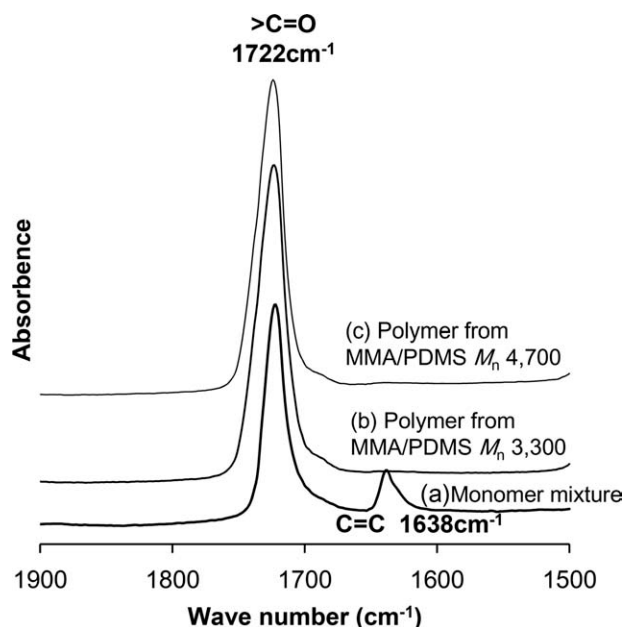
### Preparation of Crosslinked Copolymers

The comparison of the ATR-FTIR spectra between a monomer mixture from MMA and 3300 g/mol  $M_n$  PDMS macromer at a 20/80 weight ratio [Figure 2(a)], and the two types of crosslinked copolymers are shown in Figure 2. The composition of one of the crosslinked copolymers was MMA plus a 3300 g/mol  $M_n$  PDMS macromer at a 80/20 weight ratio [Figure 2(b)], and the other one was MMA and a PDMS ( $M_n = 4700$  g/mol) macromer at a 70/30 weight ratio [Figure 2(c)]. The peak signal at  $1638\text{ cm}^{-1}$ , which corresponded to the double bond from the methacryloyl group, could not be detected in the crosslinked copolymer due to the polymerization. Furthermore, any influence of the PDMS  $M_n$  on the polymerization was not observed. An example of the FTIR peak list of the crosslinked copolymer composed of MMA and a PDMS ( $M_n = 3300$  g/mol) macromer at a weight ratio of 80/20 is as follows:

**Table I.** Molecular Weight of PDMS Macromer

Code	$M_n$ from Manufacturer	$M_n$ from NMR	Results from GPC		
			$M_n$	$M_w$	$M_w/M_n$
A	1720	1700	N.D. <sup>a</sup>	<sup>a</sup>	<sup>a</sup>
B	3260	3300	3700	6700	1.81
C	4740	4500	4600	8300	1.80
E	7800	7300	6300	10,000	1.59

<sup>a</sup>Not determined.



**Figure 2.** ATR-FTIR spectra of monomer mixture and crosslinked copolymer. (a) A monomer mixture from MMA and 3300 g/mol  $M_n$  PDMS macromer at a 20/80 weight ratio. The composition of crosslinked copolymer is (b) MMA and 3300 g/mol  $M_n$  PDMS macromer at a 80/20 weight ratio and (c) MMA and 4700 g/mol  $M_n$  PDMS macromer at a 70/30 weight ratio.

2950  $\text{cm}^{-1}$  (C-H stretching), 1723  $\text{cm}^{-1}$  (C=O of ester stretching), 1435  $\text{cm}^{-1}$  (Si-CH<sub>3</sub> deformation), 1261  $\text{cm}^{-1}$  (Si-CH<sub>3</sub> deformation), 1143  $\text{cm}^{-1}$  (Si-O-Si stretching), 804  $\text{cm}^{-1}$  (Si-CH<sub>3</sub> stretching).

### DSC Measurements

The results from DSC measurements of the crosslinked copolymer formed from MMA and PDMS macromers with different

$M_n$ s (1700 and 4700 g/mol) are shown in Figure 3(A). In these crosslinked copolymers, two different  $T_g$ s were recognized. These  $T_g$ s showed constant values, which may correspond to the PMMA phase (around 124°C) and PDMS phase (around -125°C), whereas the compositions of PMMA and PDMS were varied in the crosslinked copolymer.

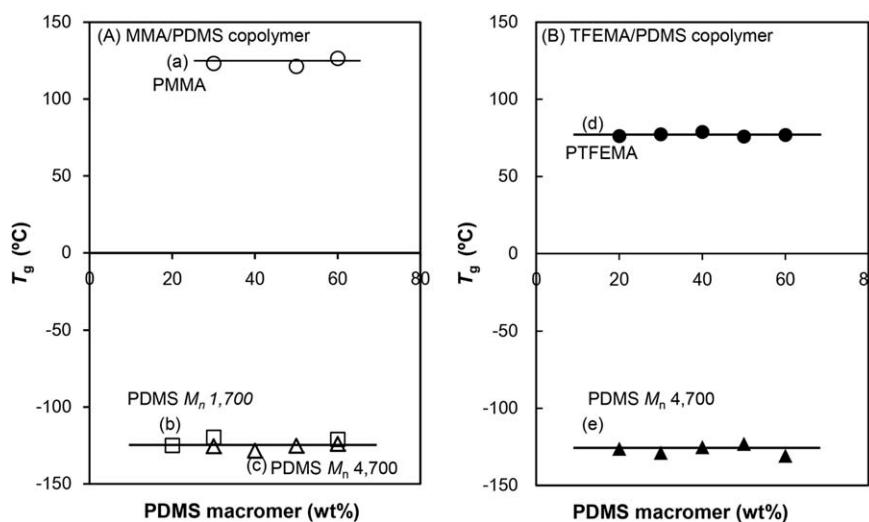
The results from the crosslinked copolymer of TFEMA/PDMS macromer with a  $M_n$  of 4700 g/mol are shown in Figure 3(B). As seen in the MMA/PDMS macromer crosslinked copolymer, two different  $T_g$ s were recognized, and showed constant values which may correspond to the PTFEMA phase (around 77°C), and the PDMS phase (around -125°C) at varied compositions.

These results imply that PMMA, PTFEMA, and PDMS are insoluble in each other over the PDMS  $M_n$  range used, and that they have phase separated internal structures.

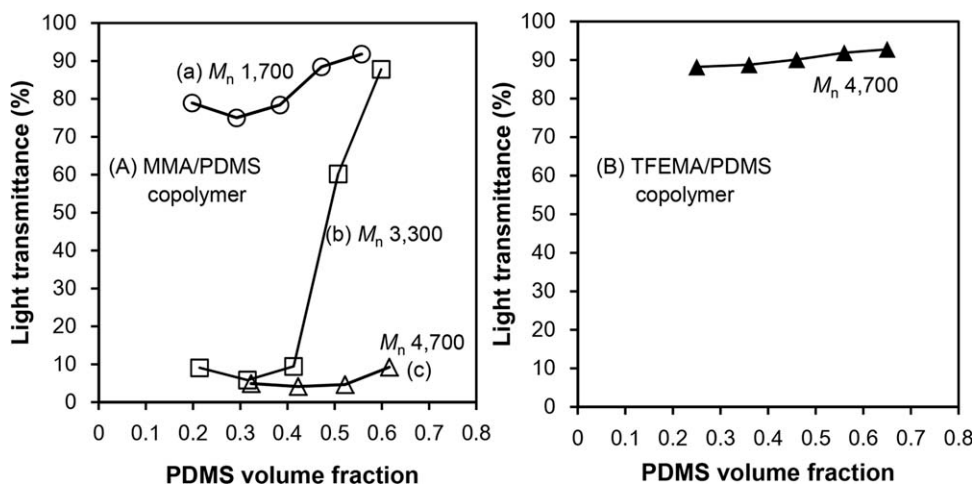
### Light Transmittance and Crosslinked Copolymer Composition

The relationship among the light transmittance of the crosslinked copolymer from MMA and PDMS macromer of 0.5 mm thickness, the PDMS volume fraction, the PDMS  $M_n$ , and the acrylic monomer is shown in Figure 4(A). The PDMS volume fraction was estimated assuming a density value of 0.98 and 1.19 for PDMS and PMMA including P1G, respectively.

Although the monomer mixture before polymerization was uniform and transparent, the light transmittance of the crosslinked copolymer composed of MMA and PDMS macromer depended on the PDMS  $M_n$  and PDMS volume fraction. A PDMS macromer of 1700 g/mol gives an almost transparent crosslinked copolymer for the measured volume fraction range [Figure 4(A) (a)]. This suggests that the size of the phase separation is sufficiently small for low light scattering, and the resultant high transparency. The crosslinked copolymer composed of a PDMS macromer at 3300 g/mol shows a drastic transmittance change



**Figure 3.** Plot of  $T_g$  of the crosslinked copolymer from methacrylate and PDMS macromer versus PDMS macromer content (wt %). (A) MMA/PDMS crosslinked copolymer. Phase of measured  $T_g$  and  $M_n$  of PDMS macromer are (a) PMMA phase and 4700 g/mol (open circle), (b) PDMS phase and 1700 g/mol (open square), (c) PDMS phase and 4700 g/mol (open triangle), respectively. (B) TFEMA/4700 g/mol  $M_n$  PDMS crosslinked copolymer. Phase is (d) PTFEMA phase (closed circle) and (e) PDMS phase (closed triangle), respectively.



**Figure 4.** Light transmittance and crosslinked copolymer composition. (A) MMA and PDMS macromer. (a), (b), and (c) represents PDMS  $M_n$  of 1700 g/mol (open circle), 3300 g/mol (open square), and 4700 g/mol (open triangle), respectively. (B) TFEMA and 4700 g/mol  $M_n$  PDMS macromer.

according to the change in the volume fraction [Figure 4(A) (b)]. Over the region where the PDMS volume fraction was less than 0.4, the appearance of the copolymer network was opaque. In contrast, a higher light transmittance was observed at a PDMS volume fraction more than 0.4. This suggests a change in morphology according to the variations of the PDMS volume fraction. In addition, crosslinked copolymers with a higher  $M_n$  PDMS [Figure 4(A) (c)] have an opaque appearance over the measured PDMS volume fraction range. This implies that a higher  $M_n$  PDMS causes a greater phase separation, resulting in light scattering even though a morphology change occurred.

In contrast to the results from the crosslinked copolymer composed of MMA and PDMS macromer, TFEMA caused a drastic improvement in light transmittance, as shown in Figure 4(B). The PDMS volume fraction was estimated assuming density values of 0.98, 1.41, and 1.19 for PDMS, PTFEMA, and P1G, respectively. The reason why TFEMA gave good transparency may be: (a) reduced light scattering at the domain boundary because of the small difference in refractive index between TFEMA and PDMS; or (b) a different morphology from the MMA/PDMS macromer composition. With regard to the former reason, we prepared crosslinked copolymer with *t*-BuMA instead of TFEMA, as *t*-BuMA has an intermediate refractive index between MMA and TFEMA as shown in Table II. The appearance of the crosslinked copolymer using MMA, TFEMA, and *t*-BuMA is shown in Figure 5, and supports the important role of the refractive index of the polymer used on the crosslinked copolymer transparency, and the advantage of fluorine-containing acrylic monomers.

#### Oxygen Permeability Coefficient and Crosslinked Copolymer Composition

The results of  $P(O_2)$  measurements on crosslinked copolymers composed of MMA and PDMS macromer are shown in Figure 6(A).

At first, we studied the contribution of the PDMS  $M_n$  to the  $P(O_2)$ . With regards to the domain size of the block copolymer, Hashimoto and coworkers reported that the domain identity

period ( $D$ ) and sphere domain radius ( $R$ ) were proportional to the  $[M_n]^{2/3}$  in styrene-isoprene block copolymers.<sup>16,17</sup> As the oxygen permeability coefficient is mainly related to the PDMS domain size in the crosslinked copolymer composed of MMA/PDMS macromer, a simple proportional calculation of the  $P(O_2)$  and a comparison between those oxygen permeability data would be useful for the estimation of the microheterophase structure of crosslinked copolymers of various PDMS molecular weights. Referring to the results from Hashimoto and coworkers, a calculation on the basis of the  $2/3$  power of the PDMS  $M_n$  between 1700 and 3300 g/mol and also between 1700 and 4700 g/mol, was performed and the results are also shown in Figure 6(A).

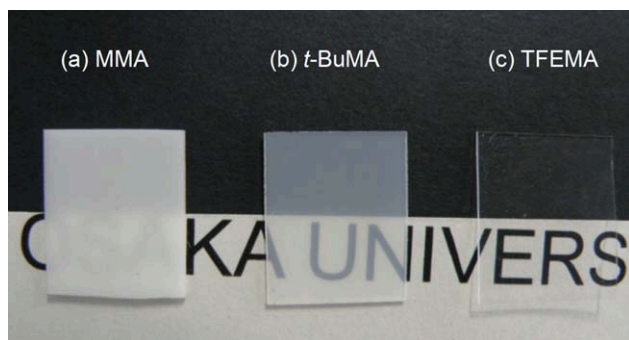
There was good agreement between the measured and calculated values for crosslinked copolymers composed of MMA and PDMS ( $M_n = 3300$  g/mol) macromer for PDMS volume fractions less than about 0.45 [Figure 6(A), (b) and (e)]. In contrast, in the case of a PDMS volume fraction larger than 0.45 and also in the case of the combination between a  $M_n$  of 1700 and 4700 g/mol, there was some difference between the calculated and measured values [Figure 6(A) (c) and (d)]. This suggests that the applicable range of this  $[M_n]^{2/3}$  theory was restricted in a sphere morphology.

The copolymerization of TFEMA instead of MMA led to drastic increases in the  $P(O_2)$  as shown in Figure 6(B). The measured data shows about a 2- or 3-fold higher value as compared with the value from the MMA crosslinked copolymer [Figure 6(a) versus (f), (c) versus (g)]. In the case of the copolymerization

**Table II.** Refractive Index of Some Polymers

Polymer	Refractive index
Methacryloyl capped PDMS ( $M_n = 4700$ )	1.408
PMMA	1.4893
PTFEMA	1.437
P- <i>t</i> -Butylmethacrylate (Pt-BuMA)	1.4638





**Figure 5.** The appearance of crosslinked copolymer with a 40(PDMS)/60(comonomer) weight ratio.  $M_n$  of PDMS macromer was 4700 g/mol and the used comonomer is (a) MMA, (b) *t*-BuMA, and (c) TFEMA. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

of TFEMA with a PDMS macromer, the influence of the  $M_n$  on the  $P(O_2)$  and the applicability of the  $[M_n]^{2/3}$  rule were studied. There was no applicability of this rule implying that this region did not correspond to a sphere type morphology [Figure 6, (g) and (h)]. With regard to the influence of fluorine-bearing compounds on the  $P(O_2)$  increase, blending the polymer from a fluorine containing vinyl monomer to PDMS or the copolymerization of a fluorine-containing vinyl monomer, MMA, and a relatively small quantity of PDMS macromer has been reported by some researchers.<sup>18,19</sup> However, one issue relates to the surface modification and the other related to the material and the condition where phase separation does not occur. For our purpose, we tried to study the relationship between copolymer morphology and the  $P(O_2)$  using model calculations.

### Calculation of $P(O_2)$ of Crosslinked Copolymer by Morphology Model

Many studies have been carried out on the relationship between morphology and gas transport in block copolymers.<sup>20–26</sup> Among the many models in this study, we noticed the method by Sax and Ottino<sup>20</sup> because of its wide applicability. As this model was developed for block copolymers without crosslinking, there may be some differences between our crosslinked material and block copolymers. However, we believe it is effective for comparative studies on the effects of morphology on bulk copolymer properties. In this method, the diffusion constant for each morphology was calculated using the following formulae.<sup>20</sup>

Sphere Model:

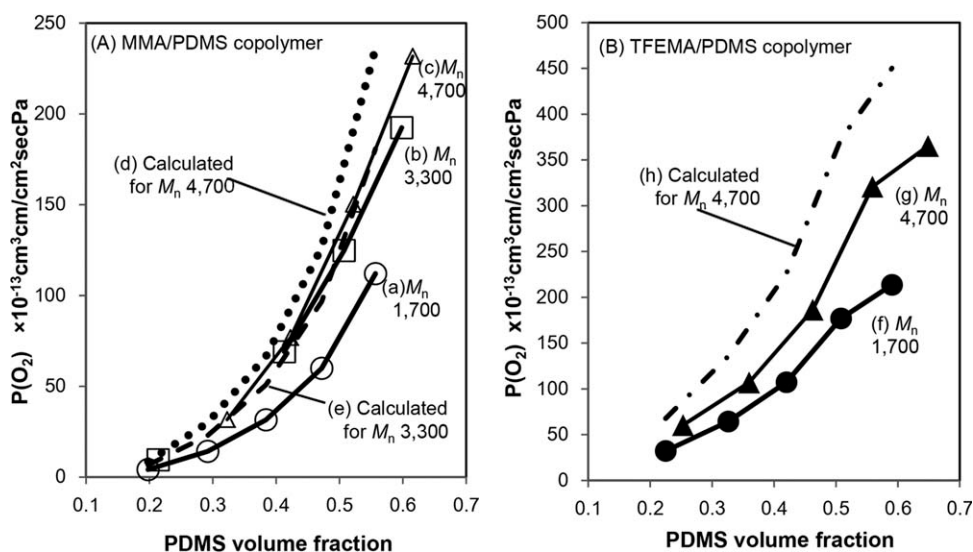
$$D_{\text{eff}} = D_c \left( 1 + 3\Phi_d \left( \frac{\bar{s}\bar{x} + 2}{\bar{s}\bar{x} - 1} - \Phi_d \right)^{-1} \right) / [\bar{s}(1 + \Phi_c(1 - \bar{s})/\bar{s})]$$

Cylinder Model:

$$D_{\text{eff}} = [\bar{s}(1 + \Phi_c(1 - \bar{s})/\bar{s})]^{-1} D_c \times \left\{ \left( \frac{1}{3} \right) \left[ (1 - \Phi_d) + \Phi_d \bar{x} \bar{s} \right] + \left( \frac{2}{3} \right) \left[ 1 + 2\Phi_d \left( \frac{\bar{s}\bar{x} + 1}{\bar{s}\bar{x} - 1} - \Phi_d \right) + 0.3 \frac{\bar{s}\bar{x} - 1}{\bar{s}\bar{x} + 1} \Phi_d^4 + 0.013 \frac{\bar{s}\bar{x} - 1}{\bar{s}\bar{x} + 1} \Phi_d^8 \right]^{-1} \right\}$$

Lamellar Model:

$$D_{\text{eff}} = D_c \left( (1/3) \left[ \left( \frac{1 - \Phi_c}{Sx} \right) + \Phi_c \right]^{-1} + (2/3) [(1 - \Phi_c)Sx + \Phi_c] \right) / S(1 + \Phi_c(1 - S)/S)$$



**Figure 6.** Oxygen permeability coefficient versus crosslinked copolymer composition. (A) Crosslinked copolymer from MMA and PDMS macromer. (a), (b), and (c) represents the crosslinked copolymer from PDMS macromer with  $M_n$  of 1700 g/mol (open circle), 3300 g/mol (open square) and 4700 g/mol (open triangle), respectively. (d) (dotted line) and (e) (broken line) represents calculated  $P(O_2)$  value according to  $[M_n]^{2/3}$  model for composition (c) based on (a), and for composition (b) based on (a), respectively. (B) Crosslinked copolymer from TFEMA and PDMS macromer. (f) and (g) The crosslinked copolymer from PDMS macromer with  $M_n$  of 1700 g/mol (closed circle) and 4700 g/mol (closed triangle), respectively. (h) (dashed line) represents calculated  $P(O_2)$  value according to  $[M_n]^{2/3}$  model for composition (g) based on (f).

**Table III.** Used Constants for the Estimation of Coefficients, PDMS<sup>a</sup>

Constant	Value	source
O <sub>2</sub> Diffusion coefficient at 25°C	16 × 10 <sup>-6</sup> cm <sup>2</sup> /s	33
Solubility coefficient at 25°C	3.1 × 10 <sup>-6</sup> cm <sup>3</sup> cm <sup>-3</sup> Pa <sup>-1</sup>	33
Activation energy	E <sub>D</sub> = 9.0 kJ/mol	34
	E <sub>S</sub> = -0.3 kJ/mol	34

<sup>a</sup>Value at 35°C was obtained using  $D = D_0 \exp(-E_D/RT)$  or  $S = S_0 \exp(-E_S/RT)$  as 18 × 10<sup>-6</sup> cm<sup>2</sup>/s, 3.09 × 10<sup>-6</sup> cm<sup>3</sup> cm<sup>-3</sup> Pa<sup>-1</sup> respectively.

where,  $D_{\text{eff}}$  is the effective diffusion coefficient,  $c$  is the continuous phase,  $d$  is the dispersed phase,  $\bar{s}$  and  $S$  represent the solubility ratio ( $S_d/S_c$ ),  $\bar{x}$  is the diffusivity ratio ( $D_d/D_c$ ), and  $\Phi$  is the volume fraction.

The solubility coefficient was also calculated.  $S_{\text{eff}}$  (effective solubility) was calculated from following formula because Thomas and coworkers<sup>21</sup> reported good agreement between the predicted and measured values with it:

$$S_{\text{eff}} = S_A \Phi_A + S_B \Phi_B$$

where,  $\Phi$  is the volume fraction,  $S$  is the solubility and  $A$ ,  $B$  are the constituents. The oxygen permeability coefficient of the sphere, cylinder, and lamellar models were calculated as follows,

$$P = D_{\text{eff}} S_{\text{eff}}$$

**Calculation of  $P$  with the Parallel Model.** The oxygen permeability coefficient of the parallel model was calculated by the following formula:

$$P = P_A \Phi_A + P_B \Phi_B$$

where  $P$ ,  $P_A$ ,  $P_B$  represent the oxygen permeability coefficients.

The diffusion coefficients and solubility coefficients of PDMS, PMMA, PTFEMA, and Pt-BuMA for the calculations were sum-

**Table V.** Used Constants for the Estimation of Coefficients, Obtained Diffusion and Solubility Coefficient for Calculation

Material	Coefficients	Source
PDMS	Diffusion, 18 × 10 <sup>-6</sup> cm <sup>2</sup> /s	
	Solubility, 3.09 × 10 <sup>-6</sup> cm <sup>3</sup> cm <sup>-3</sup> Pa <sup>-1</sup>	
PMMA	Diffusion, 0.013 × 10 <sup>-6</sup> cm <sup>2</sup> /s	
	Solubility, 0.891 × 10 <sup>-6</sup> cm <sup>3</sup> cm <sup>-3</sup> Pa <sup>-1</sup>	
PTFEMA	Diffusion, 1.01 × 10 <sup>-6</sup> cm <sup>2</sup> /s	
	Solubility, 0.891 × 10 <sup>-6</sup> cm <sup>3</sup> cm <sup>-3</sup> Pa <sup>-1</sup>	
Pt-BuMA	Diffusion, 0.108 × 10 <sup>-6</sup> cm <sup>2</sup> /s	36
	Solubility, 3.2 × 10 <sup>-6</sup> cm <sup>3</sup> cm <sup>-3</sup> Pa <sup>-1</sup>	36

marized in Tables III–V. The calculated results using these values are shown in Figure 7(A), (B), and (C).

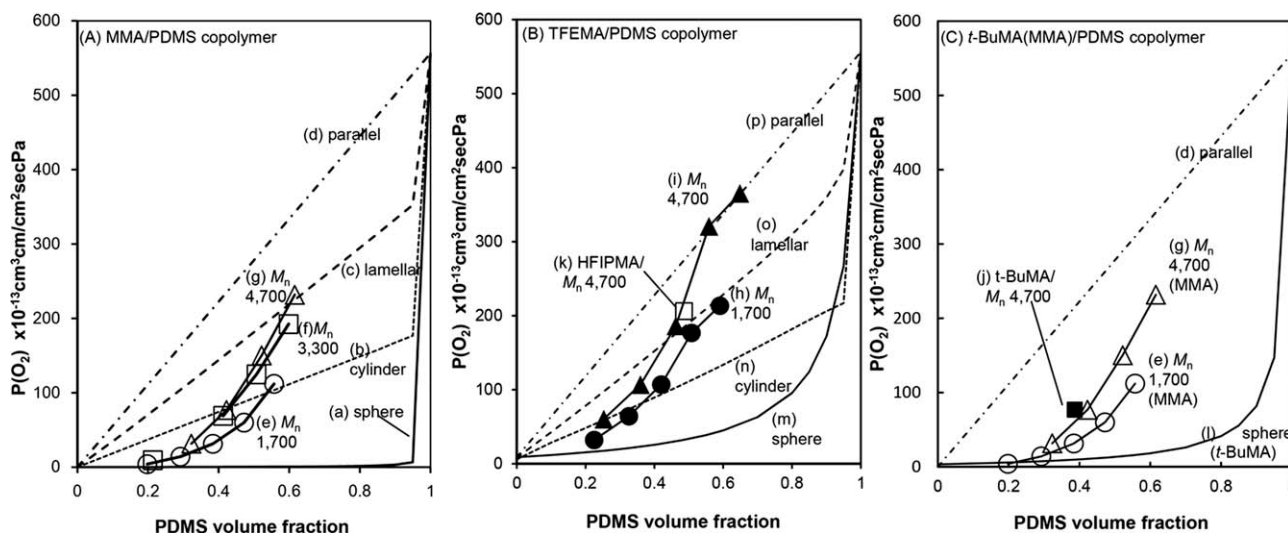
Regarding the crosslinked copolymer composed of MMA and PDMS macromer, it is recognized from Figure 7(A) that the  $P(\text{O}_2)$  values of the crosslinked copolymer with PDMS ( $M_n = 1700$  g/mol) macromer were intermediate between the sphere and cylinder models. Conversely, the  $P(\text{O}_2)$  of crosslinked copolymers at 3300 and 4700 g/mol  $M_n$  were intermediate between the sphere and lamellar models. This may correlate with the aforementioned results, which showed that the  $P(\text{O}_2)$  of the crosslinked copolymer with a 3300 g/mol  $M_n$  could be predicted from that of the 1700 g/mol crosslinked copolymer, but that of the crosslinked copolymer with a 4700 g/mol could not.

Similarly, the calculated results for the crosslinked copolymer composed of TFEMA and PDMS macromer are shown in Figure 7(B). Comparing the results from the crosslinked copolymer of MMA/PDMS macromer [Figure 7(A)] with that of the PTFEMA/PDMS macromer [Figure 7(B)], it is clear that the  $P(\text{O}_2)$  of the PTFEMA/PDMS macromer already has the structure of the parallel model at less than a 0.6 PDMS volume fraction [Figure 7 (B) (i) versus (p)]. This may be related to following factors. One may be the oxygen permeable properties of PTFEMA, even though the  $P(\text{O}_2)$  of PTFEMA is only

**Table IV.** Used Constants for the Estimation of Coefficients, Polyethylmethacrylate (PEMA)<sup>a</sup>, PMMA and PTFEMA<sup>b</sup>

Constant	Material	value	source
Diffusion coefficient at 25°C	PEMA	0.106 × 10 <sup>-6</sup> cm <sup>2</sup> /s	35
Solubility coefficient at 25°C	PEMA	0.839 × 10 <sup>-6</sup> cm <sup>3</sup> cm <sup>-3</sup> Pa <sup>-1</sup>	35
Activation Energy	PEMA	E <sub>D</sub> = 31.8 kJ	35
		E <sub>S</sub> = 4.6 kJ	35
Oxygen permeability coefficient at 34°C	PMMA	0.116 × 10 <sup>-13</sup> cm <sup>3</sup> × cm / (cm <sup>2</sup> × s × Pa)	35

<sup>a</sup>Value at 35°C for PEMA was obtained using  $D = D_0 \exp(-E_D/RT)$  or  $S = S_0 \exp(-E_S/RT)$  as 0.161 × 10<sup>-6</sup> cm<sup>2</sup>/s, 0.891 × 10<sup>-6</sup> cm<sup>3</sup> cm<sup>-3</sup> Pa<sup>-1</sup>, respectively. Ignoring the difference between 34 and 35°C, and assuming the solubility coefficient is same for both PMMA and PEMA, the diffusion coefficient for PMMA was obtained by dividing the oxygen permeability coefficient of PMMA by solubility coefficient of PEMA as 0.013 × 10<sup>-6</sup> cm<sup>2</sup>/s. <sup>b</sup>With regard to the constants for PTFEMA, following assumption was made for calculation. From the similarity of the molecular structure between EMA and TFEMA, solubility coefficient was considered to be same. The diffusion coefficient was calculated by dividing the oxygen permeability coefficient of PTFEMA [9 × 10<sup>-13</sup> cm<sup>3</sup> × cm / (cm<sup>2</sup> × s × Pa)] by the solubility coefficient.



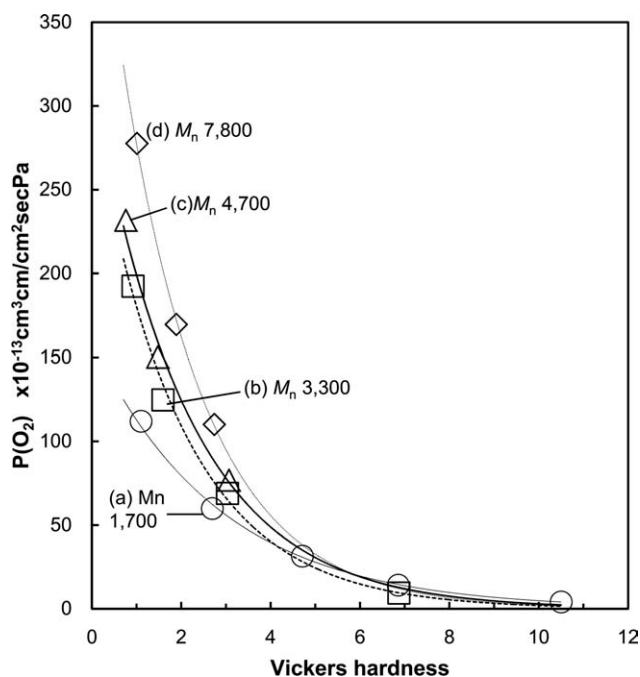
**Figure 7.** Results from calculation of  $P(O_2)$  for various morphology according to the method by Sax and Ottino.<sup>20</sup> (A) The results for MMA/PDMS crosslinked copolymer. (a), (b), (c), and (d) represents sphere model, cylinder model, lamellar model, and parallel model, respectively. PDMS  $M_n$  is (e) 1700 g/mol (open circle), (f) 3300 g/mol (open square), (g) 4700 g/mol (open triangle), respectively. (B) The results for PTFEMA/PDMS crosslinked copolymer. (m), (n), (o), and (p) represents sphere model, cylinder model, lamellar model, and parallel model, respectively. PDMS  $M_n$  is (h) 1700 g/mol (closed circle), (i) 4700 g/mol (closed triangle). The composition of (k) is HFIPMA and 4700 g/mol  $M_n$  (open square). (C) The results for additional data from *t*-BuMA/PDMS crosslinked copolymer. The composition of (j) is *t*-BuMA and PDMS with 4700 g/mol  $M_n$  (closed square). (l) represents calculated  $P(O_2)$  of sphere model for *t*-BuMA and PDMS macromer.

$9 \times 10^{-13} \text{ cm}^3 \text{ cm}/(\text{cm}^2 \text{ s Pa})$ , and low when compared with the  $556 \times 10^{-13} \text{ cm}^3 \text{ cm}/(\text{cm}^2 \text{ s Pa})$  value of PDMS. In contrast to the  $P(O_2)$  of almost zero of the MMA/PDMS crosslinked copolymer at a PDMS volume fraction of 0.2, the TFEMA/PDMS crosslinked copolymer showed a  $P(O_2)$  around  $30 \times 10^{-13} \text{ cm}^3 \text{ cm}/(\text{cm}^2 \text{ s Pa})$ , even in the case of PDMS macromer with  $M_n$  of 1700 g/mol. This situation is clearly shown in Figure 7(A) (a) versus (B) (m). Another factor may be the mutual solubility or miscibility between PTFEMA, poly(TFEMA-*co*-PDMS) copolymer, and PDMS, which are the constituents of the TFEMA/PDMS crosslinked copolymer, or similarly the solubility among PMMA, poly(MMA-*co*-PDMS) copolymer, and PDMS. In our study, according to the progress of the polymerization, a phase separation between those constituents may occur, and thus the aforementioned solubility may affect the morphology to form a parallel model structure. Furthermore, as the fluorine-containing PTFEMA has a larger specific density than PMMA, the resultant PDMS volume fraction in the crosslinked copolymer was larger in the TFEMA/PDMS crosslinked copolymer with the same PDMS macromer content on a weight basis, and this may be correlated to the difference in the relationship between the morphology and the PDMS volume fraction.

To confirm these points,  $P(O_2)$  measurements were carried out on the following samples. One sample contained *t*-BuMA as a comonomer which had a low specific density of 1.022, a somewhat low refractive index of 1.4638, and a Hildebrand solubility parameter of  $18 \text{ MPa}^{1/2}$  which is comparable to that of PMMA,<sup>27</sup> as the solubility parameters of PMMA, PDMS, and PTFEMA have been reported as 18.0–23.1,<sup>28</sup> 14.9,<sup>29</sup> and 16.4–17.3 (the values for trifluoroethylacrylate are reported)<sup>30</sup>  $\text{MPa}^{1/2}$ , respectively. Another sample had HFIPMA as a

comonomer, and this one had a high specific density (assumed to be 1.56), a low refractive index (1.39), and a low Hildebrand solubility parameter (assumed to be low from the data for hexafluoropropylene of  $10.4\text{--}14.4 \text{ MPa}^{1/2}$  or heptafluorobutylacrylate of  $15.8 \text{ MPa}^{1/2}$ ).<sup>31</sup> Furthermore, as this PHFIPMA has a higher fluorine content than PTFEMA, its  $P(O_2)$  was expected to be higher than that of PTFEMA. The results from measurements are plotted in Figure 7 as (j) and (k). It is clear that the  $P(O_2)$  from the composition containing TFEMA [Figure 7 (B) (i) and (k)]. Similarly, the  $P(O_2)$  from the composition containing *t*-BuMA is almost on the line from the composition containing MMA [Figure 7 (C)(g) and (j)]. The calculated  $P(O_2)$  from a sphere model of copolymer composed of *t*-BuMA and PDMS macromer is also shown [Figure 7(C)(l)]. There was only a small difference in the measured  $P(O_2)$  of the crosslinked copolymer composed of *t*-BuMA and PDMS macromer compared with MMA/PDMS crosslinked copolymer [Figure 7(C)(g) and (j)], although *t*-BuMA had higher calculated  $P(O_2)$  value for a sphere model than PMMA and similar one to PTFEMA as shown in Figure 7(a), (m) and (l). This implies that there is only a weak correlation between the morphology control and comonomer oxygen permeability, but rather some correlation between the crosslinked copolymer constituent's compatibility or solubility and the copolymer morphology.

Thus, this systematic study of the composition change of crosslinked copolymers composed of PDMS macromers and methacrylates revealed that the method by Sax and Ottino<sup>20</sup> was effective in understanding the great influence of the methacrylate type on the change in morphology with the PDMS volume



**Figure 8.** Plot of the measured  $P(O_2)$  versus Vickers hardness of crosslinked copolymer from MMA and PDMS macromer. The regression curve is shown as exponential function. PDMS macromer  $M_n$  is (a) 1700 g/mol (open circle), (b) 3300 g/mol (open square), (c) 4700 g/mol (open triangle), and (d) 7800 g/mol (open diamond).

fraction from the measured oxygen permeability. Furthermore, this supports the importance of the solubility or miscibility of methacrylates and PDMS on the morphology change and resultant oxygen permeability change.

#### $P(O_2)$ and Estimation of the Domain Size with the $[M_n]^{2/3}$ Model

There are very few reports describing the PDMS domain size. Akashi and coworkers<sup>32</sup> reported 6–8 nm or 10–15 nm as the domain size in Aramid–PDMS block copolymers by transmission electron microscopic observation. However, this result was from only one PDMS ( $M_n = 1680$  g/mol). More information on the PDMS domain size has been reported by Mazurek and coworkers<sup>15</sup> on the crosslinked copolymer composed of isobornyl acrylate and both end acrylamidoamidos capped PDMS. They reported 10 and 500 nm as the domain size of the copolymer from PDMSs ( $M_n = 5000$  and 10,000 g/mol, respectively), but this is somewhat peculiar from the viewpoint of  $[M_n]^{2/3}$  theory. Therefore, we tried to compare the PDMS domain sizes with different  $M_n$  values.

As stated above, the  $P(O_2)$  of crosslinked copolymer composed of PDMS with a  $M_n$  of 1700 and 3300 g/mol was proportional to  $[M_n]^{2/3}$ . Assuming that the PDMS domain shape is a sphere with a radius of  $R$ , we tried to calculate the domain size ratio. Considering that the surface of a sphere is resistance to the diffusion of oxygen, the surface area for any unit volume of a sphere is expressed as:

$$4\pi R^2 / [(4/3)\pi R^3] = 3/R$$

Therefore, the ratio of resistance to gas permeation through spheres with a radius of  $R_1$  and  $R_2$  is expressed as follows:

$$3/R_1 : 3/R_2 = R_2 : R_1$$

where  $R_1$  and  $R_2$  are the radii of domains with different PDMS  $M_n$  values.

Because the permeability coefficient is the reciprocal of the resistance to permeation, the ratio of  $P(O_2)$  from PDMS domain radii of  $R_1$  and  $R_2$  can be calculated from the ratio of the observed  $P(O_2)$  [the ratio between Figure 6(A), (a) and (b)] as follows:

$$1/R_2 : 1/R_1 = R_1 : R_2 = 1 : 1.6$$

Thus, the PDMS domain size for a  $M_n$  of 3300 g/mol is expected to be 1.6 times larger than that of PDMS with a  $M_n$  of 1700 g/mol.

#### Morphology Change of the Copolymer Network and Light Transmittance

The relationship obtained between the PDMS volume fraction and the  $P(O_2)$  may be applicable to the relationship between the morphology and the transparency. Comparing Figures 4 and 7, one can observe that there is good coincidence between the light transmittance change and the morphology change. At a PDMS volume fraction of 0.43 or so, the  $P(O_2)$  line from PDMS with a  $M_n$  of 3300 g/mol crosses the cylinder model line [Figure 7 (f) and (b)], and this may correspond to the morphology change. Conversely, Figure 4(A) (b) shows the drastic improvement in transparency at a PDMS volume fraction of around 0.43, as already described. Thus, this clearly shows the usefulness of this model calculation for understanding of the internal structure of copolymers.

#### Vickers Hardness of Crosslinked Copolymers Composed of MMA and the PDMS Macromers and PDMS $M_n$

As a measure of the practical performance of a rigid material, the Vickers hardness measurement was performed, and a plot of the oxygen permeability coefficient versus the Vickers hardness is shown in Figure 8. We observed that the higher the molecular weight of the PDMS macromer used, the higher the  $P(O_2)$  for the same Vickers hardness. The soft crosslinked copolymer tended to possess a higher oxygen permeability, which is in agreement with the higher content of PDMS macromer. Conversely, a longer Si–O–Si chain of the PDMS macromer resulted in higher gas permeability, even if it was the same hardness, suggesting a different micro phase separation.

#### CONCLUSIONS

Crosslinked copolymers with various PDMS chain lengths and two types of acrylic monomer were prepared from MMA or TFEMA, PDMS macromer and 1 G. DSC measurements of the  $T_g$  showed that PMMA or PTFEMA and PDMS were insoluble in each other. The transparency of the crosslinked copolymer composed of MMA and PDMS macromer depended on the PDMS  $M_n$ ; a higher  $M_n$  (partly 3300 g/mol, 4700 g/mol and 7800 g/mol) caused an opaque appearance, but



copolymerizing with TFEMA instead of MMA induced a drastic improvement in transparency. This could be the result of reduced light scattering due to a reduced difference in refractive index, and the copolymerization of *t*-BuMA supported this hypothesis.

In the low PDMS  $M_n$  range (1700 and 3300 g/mol), the  $P(O_2)$  was proportional to  $[M_n]^{2/3}$ , and from this relationship the domain size ratio between a  $M_n$  of 1700 and 3300 g/mol was calculated, and the ratio was found to be 1.6. This is the first proof of the relationship between domain size and the PDMS  $[M_n]$  in a crosslinked copolymer.

Copolymerization with TFEMA instead of MMA gave a surprisingly large increase in the  $P(O_2)$  of the crosslinked copolymer. To clarify the mechanism of this drastic change, a calculation of the relationship among the morphology model, PDMS volume fraction, and  $P(O_2)$  was performed. This implied that a morphology change to the parallel model occurred at a low PDMS volume fraction and was caused by some properties such as the solubility parameter and so on. This was supported by the additional measurements with *t*-BuMA and HFIPMA.

Thus, the copolymerization of a fluorine-containing acrylic monomer was found to lead to a transparency improvement, a  $P(O_2)$  increase, and therefore, fluorine-containing monomers could be expected to develop further applications in various fields.

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