Synthesis and Characterization of Ultraviolet-Curable Fluorinated Polydimethylsiloxanes as Ultraviolet-Transparent Coatings for Optical Fiber Gratings

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ABSTRACT: Synthesis of photocrosslinkable fluorinated polydimethylsiloxane (PDMS) was carried out through the direct hydrosilylation of allyl 2-(perfluorohexyl)ethyl ether with copoly(dimethyl methyl hydro siloxane). The hydrosilylation of the fluorinated allyl ether allowed the introduction of fluorinated groups onto the polysiloxane backbone. Then, a second hydrosilylation of allyl methacrylate led to PDMS bearing both fluorinated and photocrosslinkable groups. The ratio between fluorinated groups and allyl methacrylate groups allowed us to tune the refractive index of the resin without changing thermal properties. Formulations containing fluorinated PDMS were ultraviolet-cured, and their ultraviolet transparency and Yttrium Aluminium Garnet (YAG) laser resistance were investigated. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 2021–2026, 2003

Key words: polysiloxanes; fluoropolymers; photopolymerization

INTRODUCTION

The formation of Bragg gratings in optical fibers[1] is finding increasing use in a large variety of optical communications.[2] The Bragg grating consists of a local modification of the refractive index in the core of an optical fiber under ultraviolet (UV) exposure.[3] In the standard process, the polymer coating is stripped, the fiber core is irradiated, and then, the fiber is recoated. The stripping–recoating step represents a large part of the manufacturing costs. Espindola et al.[4] developed a new method that suppressed the stripping–recoating step and demonstrated the first Bragg gratings written through an UV-curable coating. This method requires the use of a UV-transparent coating with a wavelength of less than 260 nm.

To be UV transparent, materials should not contain any strong UV-absorbent groups, such as conjugated double bonds and aromatic rings. Chemical single bonds that do not have a significant UV absorbance at wavelengths less than 260 nm are C—H, C—O, C—Si, O—H, Si—O, Si—H, C—F, and C—Cl. Imamura and coworkers produced fiber gratings through the coating[5,6] and developed an aliphatic urethane acrylate UV-curable resin.[7] However, the aliphatic urethane exhibited UV absorptions between 240 and 300 nm due to carbonyl groups.

Simoff and coworkers[8,9] used aliphatic ketones as photoinitiators and showed that they can be substituted for conventional aromatic photoinitiators in UV-curable acrylate coatings. Indeed, these ketones provided a significant improvement in UV transparency. However, these aliphatic photoinitiators were much less efficient than the aromatic ones.

In the literature, different UV coatings have been tested as gratings written through coatings. An alternative to the UV-curable acrylate systems, which are UV absorbant because of carbonyl groups, is to use a UV-curable vinyl ether system.[10–13] Vinyl ether formulations were cationically UV-cured and exhibited absorbances less than 0.05 in the range 240–260 nm.. However, cationic photoinitiators were not well soluble in resin and required the use of solvent to be incorporated in the formulation.

Claesson et al.[14] studied two fluorinated polymers: Kynar 7201 and Teflon AF 1600. Kynar 7201 is a 80/20 copolymer of 1,1-difluoroethylene (CF_2=CH_2) and tetrafluoroethylene (TFE; CF_2=CF_2) produced by Atofina (Pierre=Bénite, France). The copolymer is stable under UV or other high-energy radiations and has a very low water absorption (0.02%).[15] Kynar 7201 is easily soluble in acetone, and a thin film can be made by dip-coating. Kynar 7201 films (50 μm) exhibited an absorption of 30% at 240 nm to a pulsed excimer pumped frequency doubled dye-laser at 242 nm. Teflon AF is a copolymer of

TFE and bis-2,2-trifluoromethyl-4.5-difluoro-1,3-diox-oleproduced by DuPont.[16] Teflon AF 1600 is soluble in fluorinated solvents. After dip-coating, two drying steps were needed to evaporate the solvent (300°C during 10–15 min). The films were clear and transparent. At 240 nm, the absorption was less than 5% for a film of 100 μm. At 242 nm, no pulsed laser damage was observed. Thus, the perfluorinated amorphous copolymer Teflon AF 1600 exhibited good properties for a UV-transparent coating for optical fibers, but its processing requires the use of perfluorinated solvent.

Because of Si—O, Si—C, and C—H bonds, polymethylsilsesquioxane (PMSQ) was expected to have a high UV transparency. Simoff and coworkers[17,18] demonstrated the principle of forming gratings by writing through the PMSQ polymer coating. However, PMSQ was thermally cured not UV-cured and, thus, was not compatible with the conventional fiber draw processes.

UV-curable polydimethylsiloxanes (PDMSs) were previously synthesized in our laboratory,[19–21] and the synthesis and application of photocrosslinkable PDMS were also reviewed.[22] In this study, we developed new UV-transparent curable PDMSs bearing both fluorinated side groups to increase the UV transparency and methacrylate units as UV-crosslinker groups.

EXPERIMENTAL

Materials

Copoly(dimethyl methyl hydrogen siloxane) (PDMSiH) (PS 122.5) was purchased from ABCR (Karlsruhe, Germany). 1,1,2,2-Tetrahydroperfluoro-1-octanol, 2,2,2-trifluoroethyl acrylate (ATRIFE), allyl bromide, and allyl methacrylate were purchased from Sigma-Aldrich (St. Quentin Fallavier, France) and were distilled before used. All other solvents and reagents (Aldrich) were analytical grade and were used without further purification.

The conventional urethane acrylate coating was purchased from DSM (Sittard, The Netherlands).

Instrumentation

UV spectra were recorded, from resin hand-coated on a quartz plate, with a Varian (Courtaboeuf, France) Cary 300 spectrophotometer, and IR spectra were recorded on a Nicolet (Madison, WI) 510P Fourier transform infrared (FTIR) spectrometer. NMR spectra were recorded on Bruker (Wissembourg, France) AC200 or Avance250 spectrometer with tetramethylsilane as the reference for ^{1}H-NMR. The chemical shifts are reported in part per million, where s is a singlet, d is a doublet, t is a triplet, and m is a multiplet. Unless otherwise specified, all of the spectra were recorded for CDCl$_3$ solutions. Differential scanning calorimetry

(DSC) analyses were performed under nitrogen with a PerkinElmer (Paris, France) Pyris 1 DSC apparatus calibrated with n-octane and n-octadecane. All of the samples were heated from −120 to 0°C at 20°C/min; three runs were made, and the glass-transition temperature (T_g) values were measured during the second run and confirmed by the third one, which was taken at the half-height of the heat capacity jump of the glass transition. Thermogravimetric analyses were performed in nitrogen and in air on a TGA 51 from TA Instruments (Guyancourt, France) at a heating rate of 5°C/min.

A UV Fusion system F300S (Hampshire, England) equipped with a bulb H lamp and a LC6E conveyor (speed = 20 m min^{-1}) was used to UV-cure the resins that were hand-coated on a quartz plate. The Yttrium Aluminium Garnet (YAG) laser used for the resistance test was a AVIA 355=3000 laser from Coherent (Santa-Clara, CA). Degradation was observed with a LM3 Coherent power meter.

Synthesis of fluorinated allyl ether CH$_2$=CH—O—C$_2$H$_4$—C$_6$F$_{13}$ (1)
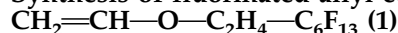
In a two-necked 500-mL flask equipped with a mechanical stirrer, 1,1,2,2-tetrahydroperfluoro-1-octanol (50.0 g, 0.14 mol) was introduced together with 250 mL of toluene, tetrabutylammonium bromide (11 g, 0.034 mol), sodium hydroxide (22.0 g, 0.55 mol), and allyl bromide (72.0 g, 0.59 mol). The mixture was heated at 110°C for 24 h. After cooling and filtration, the toluene was evaporated. **1** was purified by distillation (B_p under 20 mmHg = 69°C) and had a 62% yield.

^{1}H-NMR (CDCl$_3$, δ, ppm): 5.9 (m, 1H, CH$_2$=CH), 5.3 (m, 2H, CH_2=CH), 4.0 (d, 2H, CH$_2$=CH—CH_2), 3.7 (t, 2H, O—CH_2—CH$_2$—C$_6$F$_{13}$), 2.4 (m, 2H, O—CH$_2$—CH_2—C$_6$F$_{13}$).

Hydrosilylation of 1: Synthesis of the fluorinated copolymer (2)

General procedure: Example of the preparation of the precursor to copolymer 3a-30 whose general formula is given in Scheme 1 and which contained 30 mol% of fluorinated group and 70 mol% of methacrylic group (relative ratio, 100 z/w = 30)

1 (19.4 g, 0.05 mol) was introduced to a two-necked flask with 10 μL of a solution of 200 mg of H$_2$PtCl$_6$ in 400 mL of isopropyl alcohol. The flask was kept under a stream of argon. Through a dropping funnel, copoly-(dimethyl methyl hydro siloxane) (20.0 g, 0.02 mol) was slowly added. The mixture was stirred at 90°C for 1 night. After cooling, an equal volume of pentane was added, and the mixture was filtered over sodium sulfate, and the solvent evaporated.

^{1}H-NMR (CDCl$_3$, δ, ppm): 4.7 (s, ny H, Si—H), 3.7 (t, $2nz$ H, O—CH_2—CH$_2$—C$_6$F$_{13}$), 3.4 (t, $2nz$ H, Si—CH$_2$—CH$_2$—CH_2—O), 2.4 (m, $2nz$ H, O—CH$_2$—CH_2—C$_6$F$_{13}$), 1.6 (m, $2nz$ H, Si—CH$_2$—CH_2), 0.5 (m, $2nz$ H, Si—CH_2—CH$_2$), 0 {m, 3[6 + $n(2x + w)$] H, Si—CH_3} where $n = 13.6$, $w = 0.505$, $x = 0.495$, $y = 0.353$ and $z = 0.152$.

Hydrosilylation of allyl methacrylate: Synthesis of UV-curable fluorinated PDMSs 3a-30, 3b-50, and 3c-75 whose general formula is given in Scheme 1 and which contained 50 mol% (100 z/w = 50) and 75 mol% (100 z/w = 75) of fluorinated group respectively (relative ratio, see Table I for details)

General procedure: Example of the preparation of copolymer **3a-30**

Through a dropping funnel, a 50-mL pentane solution of allyl methacrylate (10.7 g, 0.08 mol) with hydroquinone (1 mg) and 20 μL of a solution of H$_2$PtCl$_6$ in isopropyl alcohol was introduced under a stream of argon in the last mixture, which contained fluorinated siloxane. The mixture was stirred at 55°C overnight. The disappearance of the Si—H absorption band at 2160 cm^{-1} was followed by FTIR spectroscopy. After cooling, the mixture was filtered over sodium sulfate, and the solvent evaporated.

^{1}H-NMR (CDCl$_3$, δ, ppm): 6.1 (m, ny H, CH_2=C), 5.6 (m, ny H, CH_2=C), 4.0 (m, $2ny$ H, CO—OCH_2), 3.7 (t, $2nz$ H, O—CH_2—CH$_2$—C$_6$F$_{13}$), 3.4 (t, $2nw$ H, Si—CH$_2$—CH$_2$—CH_2—O—CH_2), 2.4 (m, $2nz$ H, O—CH$_2$—CH_2—C$_6$F$_{13}$), 1.9 (s, $3ny$ H, CH$_2$=CCH_3—CO—O), 1.6 (m, $2nz$ H, Si—CH$_2$—CH_2—CH$_2$—O—CH$_2$), 0.5 (m, $2nw$ H, Si—CH_2—CH$_2$—CH$_2$—O—CH$_2$), 0.3 (m, $2ny$ H, CO—OCH$_2$—CH_2), 0 {m, 3[6 + $n(2x + w)$] H, Si—CH_3}.

For copolymer **3a-30**, $n = 13.6$, $w = 0.505$, $x = 0.495$, $y = 0.353$, and $z = 0.152$.

RESULTS AND DISCUSSION.

Recently, we described for the first time the preparation of UV-curable fluorinated PDMS with the hydrosilylation reaction.[23]

In this study, we investigated a modified procedure of that described in ref. 23. We used **1** instead of fluorinated olefin (CH$_2$=CH—CH$_2$C$_6$F$_{13}$). This fluorinated olefin was prepared from perfluorooctyl iodide through a reaction with allyl acetate followed by a deiodoacetalization.[24] **1** was synthesized by phase-transfer catalysis from 1,1,2,2-tetrahydroperfluoro-1-octanol and allyl bromide, according to the procedure described by Boutevin et al.[25]

The general procedure for the synthesis of fluorinated UV-curable PDMS is given in Scheme 1.

Commercial copoly(dimethyl methyl hydro siloxane) (PDMSiH) contained hydrosilane functional
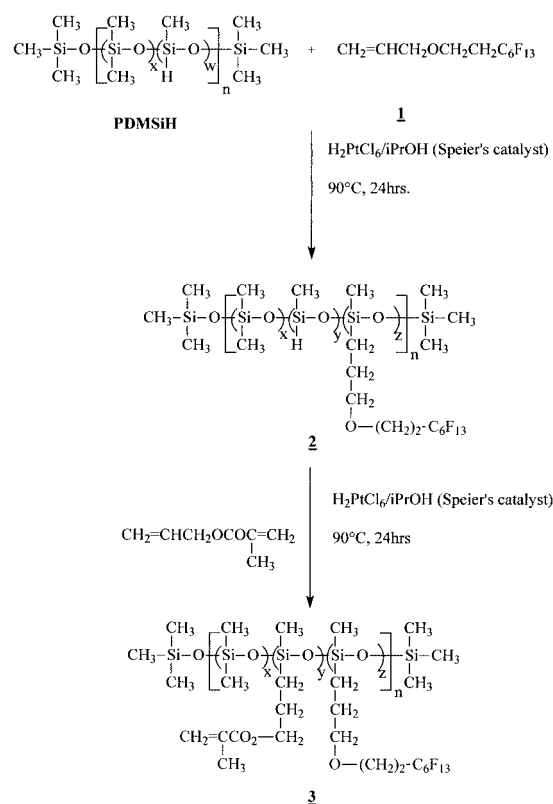
Scheme 1 Synthesis of fluorinated UV-curable PDMSs.

groups (Si—H), which could react, via hydrosilylation, to graft side groups onto the PDMS backbone to tune its physical and optical properties.

PDMSiH was a commercial product, and its structure was precisely determined with its number-average molecular weight (1050 g mol^{-1}) and by ^{1}H-NMR from the integral ratio of the Si—H signal at 4.7 ppm and the signal of the methyl groups centered at 0.1 ppm,. Thus, n was calculated as 13.6 with $x = 0.495$ and $w = 0.505$. As shown by FTIR spectroscopy, the Si—H absorption band was located at 2160 cm^{-1}, and the Si—O—Si band was at 1094 cm^{-1}.

The synthesis of the fluorinated UV-curable PDMS was performed in two steps. In the first step, PDMSiH reacted with **1** in the presence of Speier's catalyst (H$_2$PtCl$_6$, IPrOH) without solvent at 90°C for 24 h. Fluorinated poly(dimethyl methyl hydro siloxanes) (**2**'s) were obtained in quantitative yield. FTIR analysis showed that the Si—H absorption band at 2160 cm^{-1} decreased. The composition of the resulting **2** copolymers were determined by ^{1}H-NMR. Indeed, when the integral ratio of the proton signal Si—H at 4.7 ppm was compared with the integral of the methylene group at 2.4 and 3.7 ppm, corresponding to the methylene group in α and β of the fluoroalkyl group, the molar fraction of each species could be calculated. The methylene groups in α, β, and γ of the Si atom were located at 0.6, 1.7,
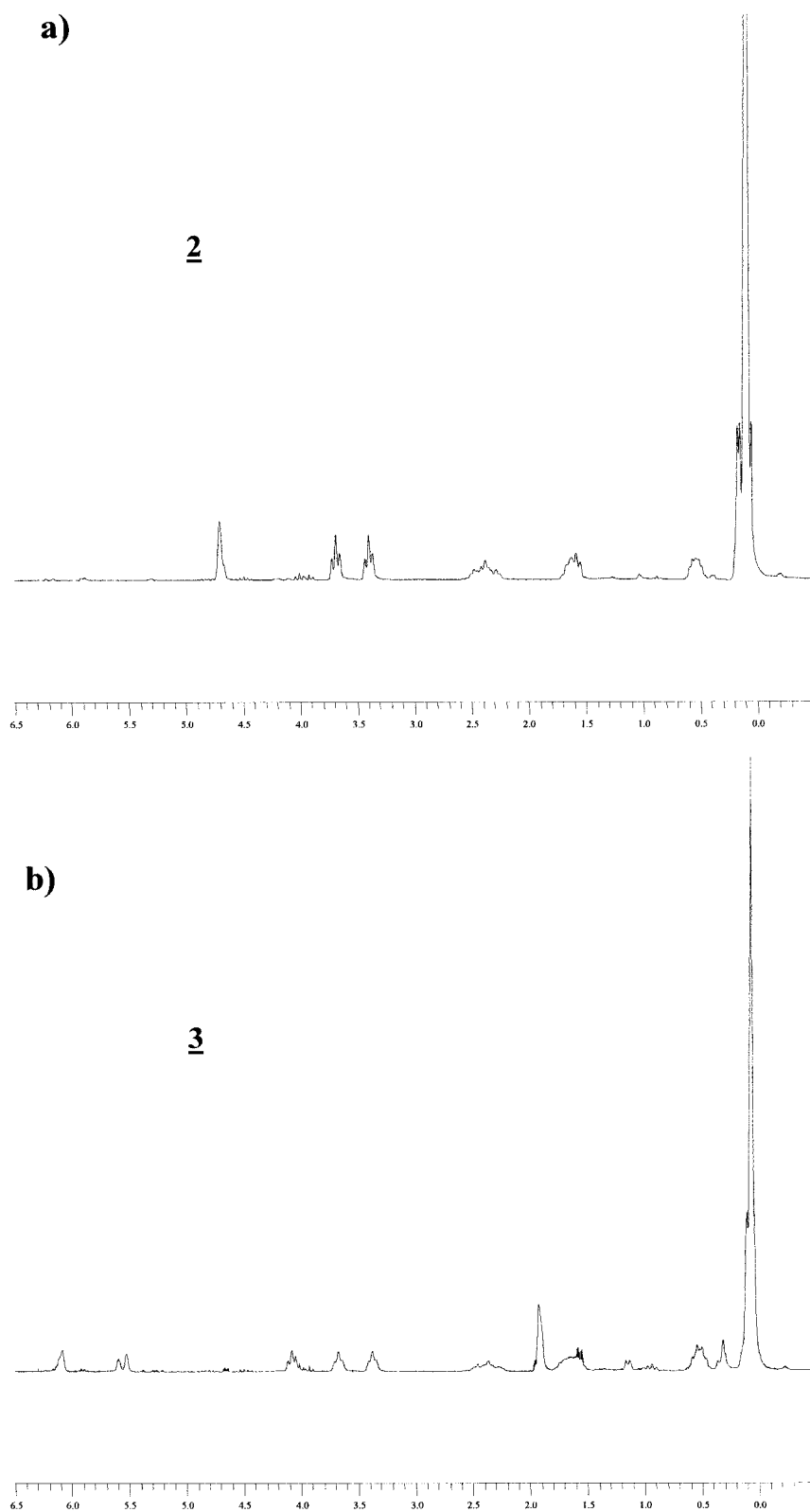
a)

2

b)

3

Figure 1 ^{1}H-NMR spectra of copolymer **3a-30** (a) before and (b) after the hydrosilylation of allyl methacrylate (solvent CDCl$_3$).

and 3.4 ppm, respectively Figure 1 shows the ^{1}H-NMR spectrum of the copolymer containing 70 mol % of unreacted SiH, which was the precursor of copolymer **3a-30**.

The second hydrosilylation reaction (step 2) involved the reaction of allyl methacrylate. In this case, the complete disappearance of the remaining Si—H bonds (2160 cm^{-1}) was followed by FTIR spectros-

TABLE I
Optical and Physical Properties of the Fluorinated UV-Curable PDMSs 3a-30, 3b-50,
and 3c-75 Compared with Those of PDMSiH

Copolymer 3	Methacrylic unit y (molar fraction)[a]	Fluorinated unit z (molar fraction)[a]	Relative ratio of the fluorinated unit (%)[b]	$T_{10\%}$ (°C)[c]	T_g (°C)[d]	Refractive index at 22°C (n_D)
3a-30	0.353	0.152	30	250	−92	1.4032
3b-50	0.252	0.252	50	260	−88	1.3964
3c-75	0.126	0.379	75	250	−91	1.3893
PDMSiH	—	—	0	—	−135	1.3999

[a] Determined by ^{1}H-NMR (see Scheme 1).
[b] 100, × $z/(z + y)$.
[c] TGA under nitrogen at 5°C min^{-1}; $T_{10\%}$ = temperature corresponding to 10% weight loss.
[d] T_g measured at 20°C min^{-1} between −120 and −20°C.

copy, and a new absorption band due to the C=O of the methacrylic unit was observed at 1729 cm^{-1}. ^{1}H-NMR analyses also showed the lack of the Si—H signal at 4.7 ppm and the characteristics signals of the methacrylic unit at 1.9 ppm (CH_3—C=CH_2—) and at 5.5–6.1 ppm (CH_3—C=CH_2—; see Fig. 1(b) for the ^{1}H-NMR spectrum of copolymer **3a-30**.

With the hydrosilylation reaction, three copolymers were prepared with different amounts of fluoroalkyl and methacrylic groups. The chemical and physical characteristics of the synthesized copolymers are given in Table I.

The thermal behavior of copolymers **3a-30**, **3b-50**, and **3c-75** with different ratios between the fluorinated and methacrylic groups was evaluated by means of DSC and thermogravimetric analysis (TGA) under nitrogen. Copolymers **3a-30**, **3b-50**, and **3c-75** exhibited thermal stability over 250°C for 10 wt % loss under nitrogen.

The relative ratio between the fluorinated and methacrylic side groups did not influence the T_g of the synthesized copolymers **3a-30**, **3b-50**, and **3c-75**, which was around −90°C. However, the incorporation of methacrylic and fluorinated side groups increased the T_g from −135°C for the starting copolymer PDMSiH to −90°C for the grafted PDMSiH copolymers **3a-30**, **3b-50**, and **3c-75**.

Figure 2 shows the influence of the fluorine content on the refractive index of copolymers **3a-30**, **3b-50**, and **3c-75**. The refractive index was very sensitive to the amount of fluorine. The refractive index of the strating PDMSiH was 1.3999, and it decreased to 1.3893 for copolymer **3c-75**, which contained 25% methacrylate units and 75% perfluorohexyl groups (relative ratio).

To measure the UV transparency of copolymers **3a-30** and **3b-50**, two resins were studied that contained a reactive diluent and a photoinitiator to prepare UV-curable coatings.

ATRIFE was used as a reactive diluent, and 2-hydroxy-2-methyl-1-phenylpropan-1-one was used as a photoinitiator. The compositions of the resins were 78.3 wt % copolymer **3a-30** or **3b-50**, 20 wt % ATRIFE, and 2 wt % photoinitiator.

The UV transmission spectrum of each UV-cured resin is shown in Figure 3 and compared with that of a conventional urethane acrylate optical fiber coating, demonstrating the superior UV transparency of the fluorinated PDMS-based resins. The UV-cured material based on copolymers **3a-30** and **3b-50** exhibited better UV transparency than the commercial coating.

Preliminary resistant laser tests were carried out with a YAG laser at 355 nm. UV-cured materials prepared from copolymers **3a-30** and **3b-50** received a laser exposure of 1200 s before degradation; the individual energy density was set to 19.8 mJ cm^{-2} at 20.6 kHz, that is, a fluence of 491 kJ cm^{-2}. By contrast, the commercial resin was not able to sustain a laser exposure of greater than 300 s. In this case, the individual energy density was set to 2 mJ cm^{-2} at 20.6 kHZ, that is, a fluence of 13.5 kJ cm^{-2}. So, the fluorinated coatings were 35 times more resistant than the commercial coating at 355 nm. The optical aspects of these coatings will be developed in a forthcoming article.

CONCLUSIONS

The synthesis of fluorinated and UV-curable PDMS was achieved through a two-step process with the
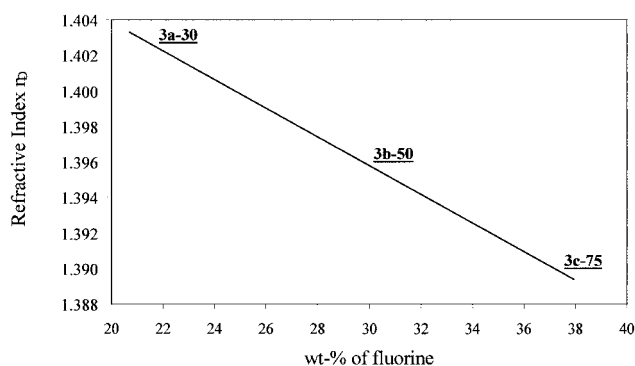

Figure 2 Refractive index at 22°C as a function of the fluorine content in copolymers **3a-30**, **3b-50**, and **3c-75**.
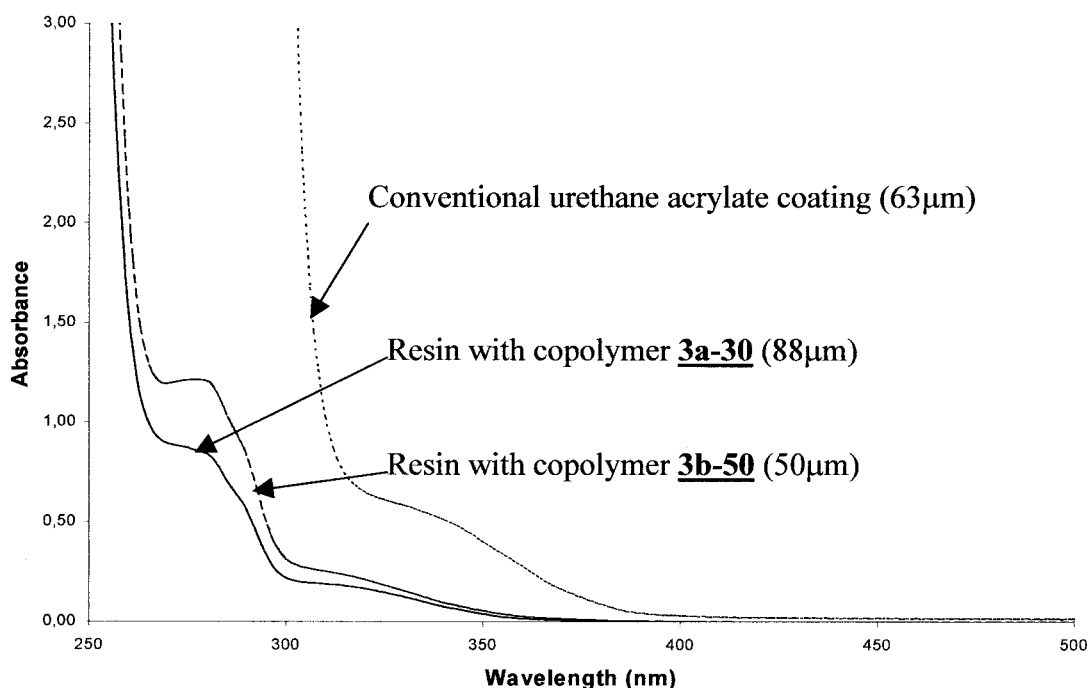
Figure 3 Absorption spectra of conventional urethane acrylate coating and UV-curable resin-based fluorinated PDMSs **3a-30** and **3b-50**.

hydrosilylation reaction. These reactions controlled the amount of **1** and allyl methacrylate groups that could be grafted on the PDMSiH backbone. The relative ratio between fluorinated and methacrylics groups tuned the refractive index values and preserved the heat resistance properties, and the T_g increased compared to that of PDMSiH. The resulting copolymers exhibited low refractive indices. The resins formulated with the new oligomers yielded films with a low UV transparency and a good resistance to YAG laser exposure at 355 nm.

References

1. Hill, K. O.; Fujii, Y.; Johnson, D. C.; Kawasaki, B. S. Appl Phys Lett 1978, 32, 647.
2. White, A. E.; Grubb, S. J. In Optical Fiber Telecommunication; Koch, T. L.; Kaminov, I. P., Eds.; Academic: New York, 1997; Vol. IIIB, Chapter 7, p 267.
3. Uarela, D.; Costantini, D. M.; Limberger, H. G.; Salathe, R. P. Opt Lett 1998, 5, 397.
4. Espindola, R. P.; Atkins, R. M.; Simoff, D. A.; Nelson, K. T.; Paczkowski, M. A. Presented at the Optical Fiber Conference OFC'97, Dallas, TX, 1997.
5. Imamura, K.; Nakai, T.; Sudo, Y.; Imada, Y. Electron Lett 1998, 34, 1772.
6. Imamura, K.; Nakai, T.; Moriura, K.; Sudo, Y.; Imada, Y. Electron Lett 1998, 34, 1016.
7. Lio, T.; Hosotani, K.; Kuzushita, H.; Genji, T.; Imamura, K. In International Wire Cable Symposium Proceedings; 1999; p 714.
8. Simoff, D.; Paczkowski, M. A.; Ragan, R.; Palmer, A. Proceedings of RadTech International, North America, 1998; p 42.
9. Chandross, E. A.; Paczkowski, M. A.; Simoff, D. A. (to Lucent Technologies, Inc.). U.S. Pat. 5,773,486 (1998).
10. Simoff, D. A.; Espindola, R. P.; Paczkowski, M. A.; Atkins, R. M.; Wang, N. P.; Hale, A. Polym Prepr (Am Chem Soc Div Polym Chem) 1999, 40, 1289.
11. Espindola, R. P.; Atkins, R. M.; Wang, N. P.; Simoff, D. A.; Paczkowski, M. A.; Windeler, R. S.; Brownlow, D. L.; Shenk, D. S.; Glodis, P. A.; Strasser, T. A.; DeMarco, J. J.; Chandonnet, P. J. IEEE Photonics Technol Lett 1999, 11, 833.
12. Houlihan, F. M.; Paczkowski, M. A.; Simoff, D. A.; Varlemann, U.; Wang, N. P. (to Lucent Technologies, Inc.). Eur. Pat. 990,625 (2000).
13. Blyler, L. L.; Paczkowski, M. A.; Simoff, D. A.; Varlemann, U.; Wang, N. P. (to Lucent Technologies, Inc.). U.S. Pat. 5,989,627 (1999).
14. Claesson, A.; Sahlgren, B.; Fokine, M.; Stubbe, R. International Wire Cable Symposium Proceedings; 1997; p 82.
15. Tournut, C. Macromol Symp 1994, 82, 99.
16. Korinek, P. M. Macromol Symp 1994, 82, 61.
17. Simoff, D. A.; Paczkowski, M. A.; Ragan, R.; Inniss, D.; Strasser, T. A.; Borick, J. M.; Peedrauani, J. R.; Espindola, R. P.; Atkins, R. M.; Nelson, K. T.; Aspell, J. H.; Kuch, V. J. International Wire Cable Symposium Proceedings; 1997; p 86.
18. Aspell, J.; Inniss, D.; Kuck, V. J.; Paczkowski, M. A.; Simoff, D. A. (to AT&T Corp.). Eur. Pat. 762,158 (1997).
19. Abdellah, L.; Boutevin, B.; Youssef, B. Eur Polym J 1991, 27, 695.
20. Abdellah, L.; Boutevin, B.; Youssef, B. Eur Polym J 1991, 27, 821.
21. Boutevin, B.; Abdellah, L.; Dinia, M. Eur Polym J 1995, 31, 1127.
22. Abdellah, L.; Boutevin, B.; Youssef, B. Prog Org Coat 1994, 23, 201.
23. Boutevin, B.; Guida-Pietrasanta, F.; Ratsimihety, A. J Polym Sci Part A: Polym Chem Ed 2000, 38, 3722.
24. Ameduri, B.; Balague, J.; Boutevin, B.; Caporiccio, G. J Fluorine Chem 1997, 11, 843.
25. Boutevin, B.; Pietrasanta, Y.; Youssef, B. J Fluorine Chem 1997, 34, 167.