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8. Novel Fluoropolymers for Next Generation Lithographic Material

- Relationship between Structure and Performances -

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Two kinds of fluorodiene that were derivatives of our original monomer and novel fluoropolymers from those monomers were synthesized for next generation lithographic material. The polymers obtained by cyclopolymerization possessed good transmittance at 157nm and 193nm wavelengths due to fluorine atoms in them. Various physical measurements showed the polymers had both advantage and disadvantage. The one had good dissolution character to standard developer but inadequate heat resistance, and conversely, the other did inadequate dissolution character but high heat resistance for application to resist polymer. It turned out that the new monomers were possible to be used as a comonomer for resist polymer and some physical characters of the former polymer and FPR were good enough for top coat material for 193nm immersion lithography.

1. Introduction

In microelectronic industry, photolithography is an important patterning technology and is the key process for fabricating semiconductors. To achieve higher accumulation on integrated circuit responding to the market demand for higher performance devices, shorter wavelength light has been adopted in the process successfully to form finer pattern on silicon wafer.

157nm lithography, a next generation lithographic technology, has been developed for production of semiconductors at 65nm node or below. There are some remaining obstacles, and development of resist materials is one of the major issues of them. The important features required for the resist material are; high transparency at 157nm wavelength, good dissolution behavior to developer, dry etching resistance, and heat resistance. Numerous researches revealed that the introduction of fluorine atoms to polymers was

essential, and alicyclic fluoropolymer was found to be the best candidate as a base polymer for single layer resist⁽¹⁾⁻⁽⁵⁾.

We have already developed two series of fluoropolymers 'FPR' (Fig. 1)⁽³⁾⁽⁴⁾ and 'ASF'⁽⁵⁾⁽⁶⁾ which have high transparency of absorption coefficient $<0.5 \mu\text{m}^{-1}$ in last three years. On FPR, it has good transparency and heat resistance. However its dissolution rate was inadequate and is in need of improvement.

It was found that a little structural difference of monomer affected polymer performance in development of ASF⁽⁵⁾. On the other hand, FPR monomer has heptadiene backbone and gives 5- and 6-membered rings by cyclo-polymerization. If the number of carbon atoms in monomer backbone is changed, the conformation of polymer and/or the surroundings of functional groups should also change. It is considered that these changes affect polymer performances. We newly synthesized two monomers which were derivatives of FPR

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monomer⁽³⁾ for improvement of FPR's weak point, its dissolution behavior.

Recently, 193nm immersion technique, the rival candidate to 157nm lithography, has rapidly been developed. Cover materials of resists, so-called 'top coat' for immersion system require firstly insolubility to water (immersion medium), and the similar characters to the requirements of a resist, i.e. high transmittance at 193nm, solubility to developer.

In this report, the influences of carbon number in monomer backbone to polymer performances are discussed in the cases of elongation from heptadiene (FPR monomer) to octadiene and shortening to hexadiene.

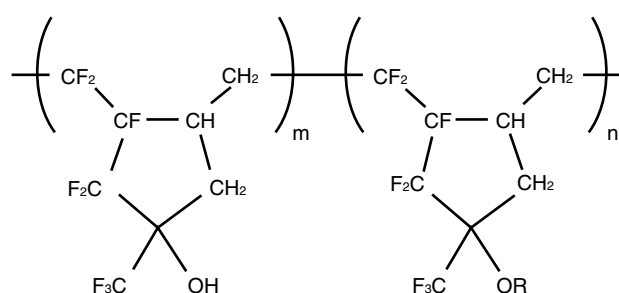


Fig. 1 Chemical structure of FPR. Bare polymer (R=H) was studied in this report.

2. Experimental

2.1 Synthesis

NMR spectra were recorded on JEOL JSM-AL300 spectrometer (300MHz). Tetramethylsilane and trichlorofluoromethane were used as internal standard for ¹H and ¹⁹F, respectively.

1,1,2,3,3-Pentafluoro-4-trifluoromethyl-4-hydroxy-1,6-heptadiene [M]

The synthesis of [M] was described elsewhere⁽⁷⁾⁽⁸⁾. The intermediate of [M], 1,2-dichloro-octafluoro-4-pentanone was produced by our own fluorination method utilizing difluorine gas⁽⁹⁾.

1,1,2,3,3-Pentafluoro-4-trifluoromethyl-4-hydroxy-1,5-hexadiene [M - 1]

The monomer [M - 1] was synthesized from the same intermediate mentioned above and in almost the same way as [M]. Exception is to use vinylmagnesium bromide instead of allylmagnesium chloride in grignard reaction step. [M - 1]; bp. 48 to 49 / 8.0kPa; ¹H NMR (300.4MHz, CDCl₃) 2.98 (br, 1H), 5.72 (d, 1H), 5.88 (d, 1H), 6.02 (m, 2H); ¹⁹F NMR (282.7MHz, CDCl₃) - 76.6 (m, 3F), - 92.8 (m, 1F), - 107.2 (m, 1F), - 114.3 (m, 2F), - 183.4 (m, 1F).

1,1,2,3,3-Pentafluoro-4-trifluoromethyl-4-hydroxy-1,7-octadiene [M + 1]

The monomer [M + 1] was also synthesized from the same intermediate and in the same way as monomer [M - 1] using 3-butenylmagnesium bromide. [M + 1]; bp. 46 to 47 / 1.1 kPa; ¹H NMR (300.4MHz, CDCl₃) 2.04 (t, 2H), 2.33 (q, 2H), 2.99 (br, 1H), 5.17 (dd, 2H), 5.84 (m, 1H); ¹⁹F NMR (282.7MHz, CDCl₃) - 76.0 (m, 3F), - 92.4 (m, 1F), - 107.1 (m, 1F), - 113.6 (m, 2F), - 184.4 (m, 1F).

2.2 Polymerization

All polymers were obtained by solution polymerization under usual radical polymerization condition. Polymerization reaction was carried out for 18 hours in nitrogen atmosphere. Ethyl acetate and HCFC R-225 (C₃H₂F₅Cl₂) were selected as solvents and monomer concentrations were in the range from 20 to 40wt% to the solution. The reaction temperatures were 20, 40, and 70 at which perfluorobutyric peroxide (PFB), diisopropyl peroxy dicarbonate (IPP), and perfluorobenzoic peroxide (PFBPO) were used as radical initiator respectively. Initiator concentration was 1.5wt% to the solution on all the polymerizations. After polymerization reaction, obtained polymer solution was dropped into large excess of hexane for purification, and the precipitated polymer was dried in a vacuum at 80 for 24 hours.

2.3 Measurement

Polymer structure was confirmed by ¹H and ¹⁹F NMR (see section 2.1). Gel permeation chromatography (GPC) was performed on TOSOH HLC-8220 chromatograph at 40 with THF as an eluent. From the GPC result, the number average molecular weight (M_n) and weight average molecular weight (M_w) were determined by calibration with poly(styrene) standard. Differential scanning calorimetry (DSC; Perkin-Elmer DSC7 or Seiko Instruments Inc. DSC6220) was also used for the analysis of thermal behavior of the polymers (heating rate = 10 /min). Dynamic thermogravimetry (TGA) of the polymers was performed under nitrogen atmosphere with MAC Science Co., Ltd. TG-DTA2000SA thermogravimeter at a heating rate of 10 /min. Films of polymers were obtained from 10wt% polymer solution in propyleneglycol monomethyl ether acetate solution by spin-coating (2000rpm for 30 seconds) on silicon wafer or CaF₂ plate followed by baking at 90 for 120 seconds. Film thickness was measured with thin-film measurement system (FILMETRICS, INC).

Filmetrics F20). VUV absorption spectra of the polymers were measured with Bunkoh-Keiki Co.,LTD. KV-201AD. Dissolution behavior was checked by immersing a film of polymer into standard developer, aqueous 2.5wt% tetramethyl ammonium hydroxide (TMAH) solution for 15 or 30 seconds, followed by measuring its film thickness. The percentage of remained film thickness was evaluated compared to its original thickness. Refractive index was measured by J. A. Wollam Japan with fast spectrometric ellipsometer (J. A. Wollam Japan M-2000D).

2.4 Computational

The ideal unit structures for calculations (see below) and head to tail sequence were selected as a model structure on each polymer for convenience. Structure optimization of the model polymer was carried out by Materials Studio (Accelrys Inc.) with an eicosamer of the selected unit structures.

Solvent excluded surface was calculated by GEOPOL93 program⁽¹⁰⁾ based on Richard's model⁽¹¹⁾ with a water molecule of 0.169nm radius as an accessing solvent molecule to polymers. We focused on the ratios of surface area of hydroxyl group to whole polymer surface area for solubility consideration.

3. Results and discussion

Comparing the two types of ASF polymer structures (ASF-1 and ASF-2)⁽⁵⁾⁽⁶⁾, the existence of the one CH₂ unit in side chain was found to affect the performance as a resist, especially their dissolution behavior⁽⁶⁾. This seemed to be brought about by the difference of hydroxyl group surroundings. It is possible to improve polymer performances with such a little structural difference of monomers.

The weak point of our first generation resist polymer 'FPR' was its low dissolution rate to a developer. Therefore, syntheses and polymerizations of its two derivative monomers were carried out in order to improve its dissolution behavior. The effects of the change of the unit structure to polymer performances as a resist polymer were studied. The derivative monomers were 1,1,2,3,3-Pentafluoro-4-trifluoromethyl-4-hydroxy-1,5-hexadiene [M - 1] and 1,1,2,3,3-Pentafluoro-4-trifluoromethyl-4-hydroxy-1,7-octadiene [M + 1] whose structures are shown in Fig. 2. They have the difference of the number of CH₂-unit compared with FRP monomer.

ArF immersion lithography has been developed

rapidly for the last two years. The coating material of a resist, so-called 'top coat' is need to be developed to prevent immersion medium and resist from contaminations⁽¹²⁾. For example, leaching of photoresist and/or additives into immersion medium leads to optical changes in the medium and contaminations of the lens. The required properties for top coat partially resemble to 157nm resist. These led us to study application to top coat for 193nm material as well as 157nm resist.

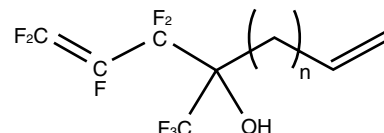


Fig. 2 The structure of the monomers. [M - 1] (n=0), [M] (n=1), and [M + 1] (n=2).

3.1 Modeling study

Firstly, the optimized structure of polymer models was calculated by computation as a preliminary investigation before synthesis of monomers. The eicosamer structures of the ideal structures of each unit (Fig. 3) were adopted as models of polymers for optimization. These calculation contained (S)- and (R)- form unit structure randomly with the same probability because racemic mixture of each monomer should be obtained from grignard reaction step in actual synthetic route as described below. The head to tail sequence was selected for simplification.

As a result, all the model polymers were in helical structure (Fig. 3). The pitch and the turning radius of the helix were found to be smallest in [P - 1]. Additionally, the arrangement of hydroxyl group was best-ordered in [P - 1].

Solvent excluded surfaces of the model polymers were calculated to estimate accessibility of a solvent, in another words, TMAH aqueous solution developer. The ratio of surface area of hydroxyl group to whole polymer surface area was considered to be good indicators of solvent accessibility to hydroxyl group and, furthermore, dissolution character of a polymer. The calculated ratios of these solvent accessibilities were 1.11, 1, and, 0.73 on [P - 1], [P], and [P + 1] respectively, based on accessibility of [P] as an unity. This suggests [P - 1] has a potential of better dissolution character than [P] and [P + 1] does that of worse character.

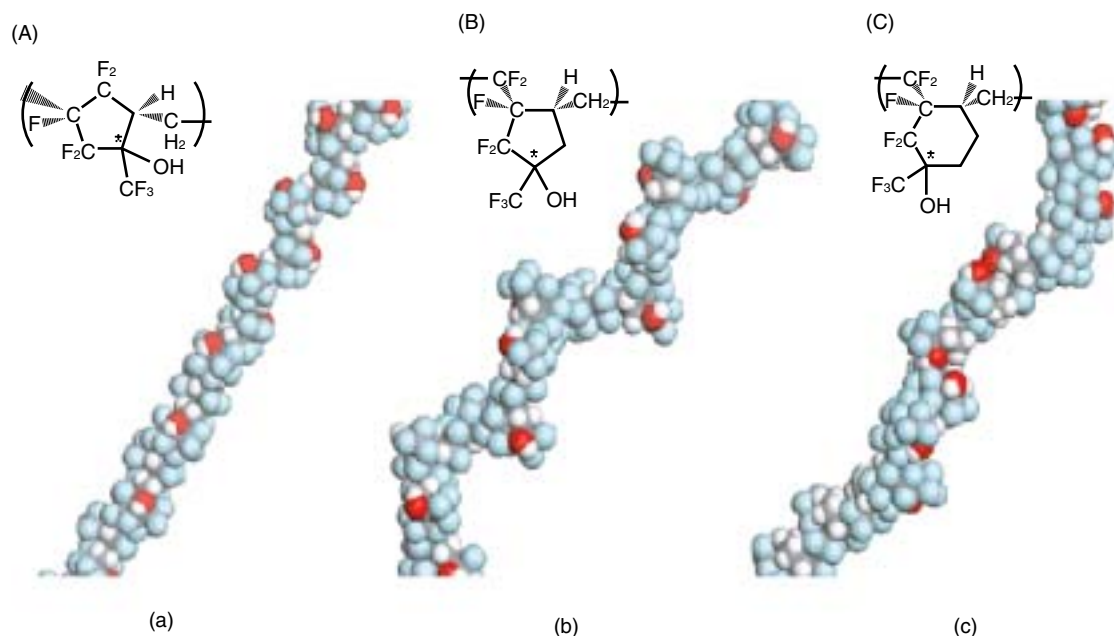
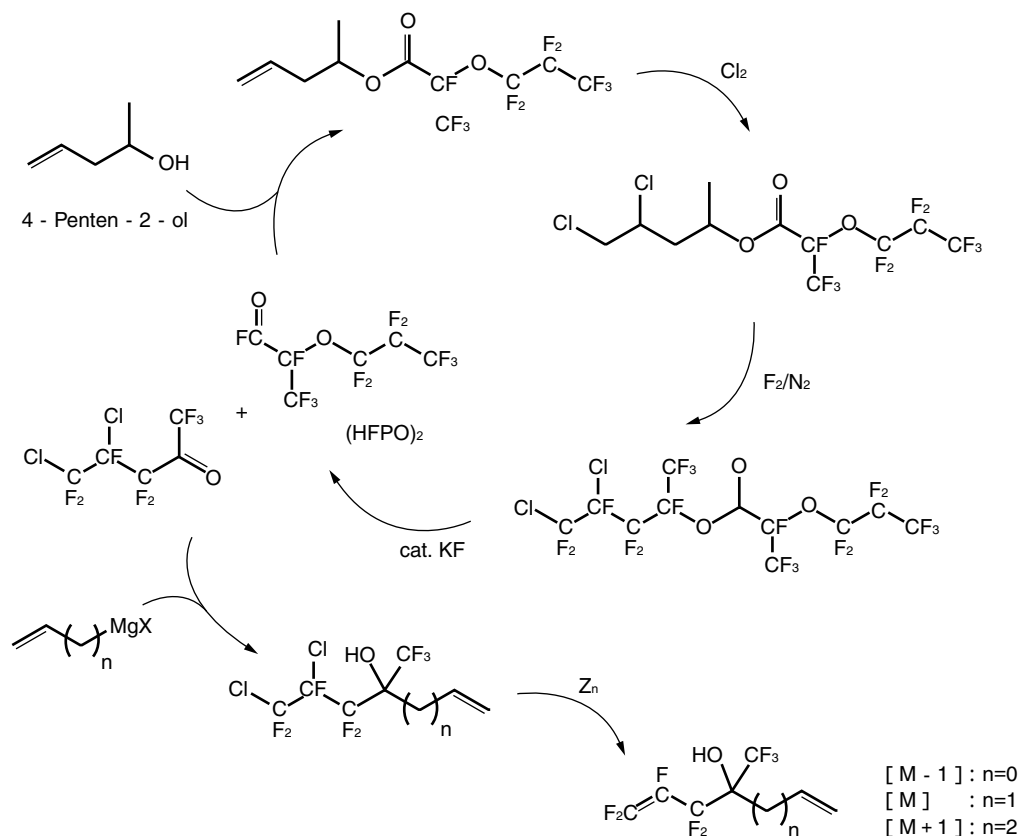


Fig. 3 The selected unit structures of [M - 1] (A), [M] (B), and [M + 1] (C) and corresponding optimized eicosamer structures of [M - 1] (a), [M] (b), and [M + 1] (c). Hydrogen atoms, carbon atoms, oxygen atoms (hydroxyl oxygen) and fluorine atoms are appeared as balls in white, gray, red and sky blue, respectively.

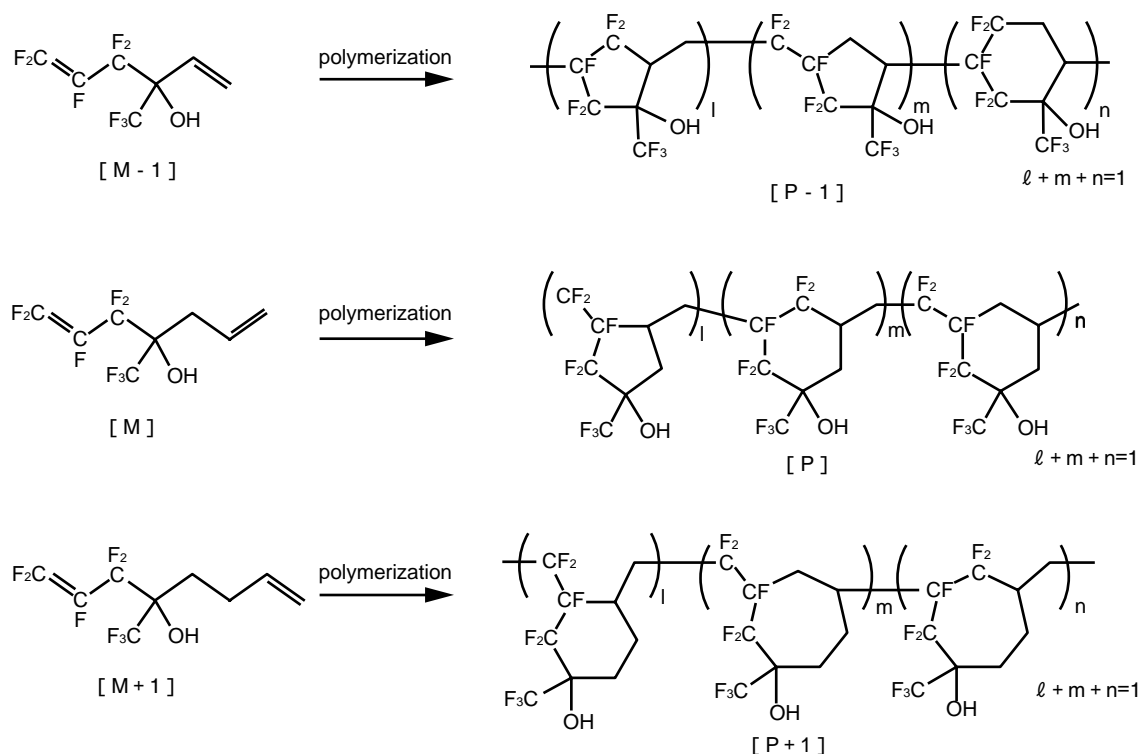
3.2 Synthesis and polymerization

We synthesized a partially fluorinated asymmetric diene, 1,1,2,3,3-Pentafluoro-4-trifluoromethyl-4-hydroxy-1,6-heptadiene [M] (a

monomer of FPR) and two derivatives of it. Scheme 1 shows the synthetic route to the monomers. The important intermediate of [M], 1,2-dichloro-octafluoro-4-pentanone was produced with



Scheme 1 General synthetic route to the monomers.



our own fluorination method 'PERFECT'⁽⁹⁾ that utilized fluorine gas directly. All the reactions in the scheme were completed in moderate yield or almost quantitatively. The other monomers, 1,1,2,3,3-Pentafluoro-4-trifluoromethyl-4-hydroxy-1,5-hexadiene [M - 1], and 1,1,2,3,3-Pentafluoro-4-trifluoromethyl-4-hydroxy-1,7-octadiene [M + 1] were also synthesized from the same intermediate.

Although the cyclopolymerization of various hydrocarbonic dienes is well known⁽¹³⁾, that of fluorinated dienes has been scarcely reported⁽¹⁴⁾. Not only the existing monomer [M] but the new monomer [M - 1] and [M + 1] were easily cyclopolymerized under usual radical polymerization condition. Purification and drying after the solution polymerization gave solvent-soluble white solid polymers [P] (FPR), [P - 1], and [P + 1] from the monomer [M], [M - 1], and [M + 1] respectively (Scheme 2).

3.3 Polymer properties

The polymers whose molecular weights were about 20,000 were obtained in good yield (>80%) by standard radical polymerization condition (Table 1). No gel formation was observed on three polymers. Moreover on [M], no gel formation was occurred even by bulk polymerization and no residual C-C double bond was observed in [P] by IR spectroscopy measurement. These polymers are

easily soluble in common organic solvents; methanol, acetone, ethyl acetate, tetrahydrofuran, propyleneglycol monomethyl ether acetate, and partially soluble in R-225. Solubility in common solvents is important for spin-coating onto silicon wafer in practical usage as a resist polymer. Taken Mw/Mn values into account, it seemed that there was no or little intermolecular crosslinking occurred in the polymers.

3.3.1 The unit structure in polymers

The polymer [P] was confirmed by ¹⁹F NMR to contain one kind of 5-membered and two kinds of 6-membered rings formed by cyclopolymerization. As the case of [P], [P - 1] is expected to contain two kinds of 5-membered ring and one kind of 6-membered ring (energetically less favorable 4-membered ring won't generate.) (Scheme 2). Unfortunately it was too complicated to analyze the composition of ring size in [P - 1] by NMR. On about [P + 1], it supposedly consists of mainly one kind of 6-membered ring, and two kinds of 7-membered ring. The difference of unit structure should affect conformation of polymers, which should cause the change of polymer performances.

¹H NMR spectra of [P - 1] showed its interesting structural feature. The signal ascribed from hydroxyl proton in [P - 1] was split in four in the range from 7.5ppm to 8.0ppm (7.51, 7.66, 7.80, and 7.95). This splitting strongly indicates existence of

Table 1 Properties of the Polymers.

	Initiator	Mw	Mw/Mn	Td [°C]	Tg [°C]	Abs. ^(a) at 157nm [μm^{-1}]	Dissolution character (to developer)
[P - 1]	PFB	18200	1.87	> 400	85	0.48	good
[P]	IPP	22000	2.45	> 400	150	0.40	good
[P + 1]	PFB	17700	2.11	> 400	169	0.58	bad

(a) Absorption coefficient

four types of hydroxyl group whose surroundings are significantly different each other⁽¹⁵⁾.

3.3.2 Heat resistance

The 20% decomposition temperatures Td(20) of the polymers were above 400 °C (Table 1), almost the same as the other cyclic fluoropolymers⁽³⁾⁽⁵⁾. Heat resistance as a lithographic material is evaluated with its glass transition temperature Tg. High Tg (120 °C <) was preferable to baking step in lithography process. Tg of [P - 1], [P], and [P + 1] were 85 °C, 150 °C, and 168 °C, respectively (Table 1). This result as qualitatively expected indicated the order of the flexibility of the polymers. That is the same order as steric bulkiness of the cyclic unit structure projecting from main chain of each polymer. It seems that bulkier ring suppresses polymer segmental motion at higher temperature. [P] and [P + 1] has Tg high enough as a resist base polymer and all of the polymer including [P - 1] has Tg high enough as a top coat for 193nm immersion.

3.3.3 Transmittance

Transparency is one of the most important characters for resist polymer. But only a few materials have been developed to possess its absorption coefficient of $< 1.0 \mu\text{m}^{-1}$ at 157nm wavelength up to now⁽²⁾⁽³⁾⁽⁵⁾. The results measured with films of obtained polymers showed good transparency at 157nm of absorption coefficient around $0.5 \mu\text{m}^{-1}$. The terminal effect attributed to the initiator was appeared on [P + 1] despite its high Mw compared to the mass of the initiator. The absorption coefficient of the [P + 1] polymer obtained with IPP was indeed, $0.66 \mu\text{m}^{-1}$, $0.08 \mu\text{m}^{-1}$ higher than [P + 1] with perfluoroinitiator PFB shown in Table 1.

Low transmittance of [P + 1] is understandable because of its relatively low fluorine content, following a general rule. However, transparency of [P - 1] whose fluorine content is relatively high is almost the same or a little lower than that of [P]. The simulation work⁽¹⁶⁾ predicted that the specific position of fluorine effectively worked for high transmittance. Taken these results into account, the fluorine atoms in [M - 1] might not be introduced in effective positions in this backbone

for high transmittance.

On transmittance at 193nm for top coat, all three polymers were extremely transparent of $< 0.05 \mu\text{m}^{-1}$ at 193nm due to fluorine atom in the polymers (Table 2). Especially, that of [P - 1] was excellent and followed a general rule mentioned. Significant difference was not seen on terminal effect from initiator.

3.3.4 Dissolution character

Though hydroxyl group was introduced to [M] in order to bring about solubility, [P] based resist was inadequate on this character and the dissolution rate was slightly low to use practically. To evaluate the solubility to TMAH solution, the films of the polymers obtained by spin-coating were immersed into TMAH solution. After the immersion, the film thickness was measured and compared with the thickness before immersion.

We found that the changes of unit structure gave the drastic effect on solubility to standard developer, TMAH solution. Although the films of both [P - 1] and [P] completely dissolved in 15 seconds, in the case of [P + 1] 87% of the film remained after 15 seconds immersion and 78% remained after 30 seconds immersion. This results showed their difference of dissolution character (Table 1). [P - 1] and [P] were easily soluble to developer, and conversely [P + 1] was difficult to solve compared with them. In a preliminary test (data not shown), [P - 1] was much more soluble than [P] as expected from the calculated solvent excluded surfaces ratio of hydroxyl oxygen. The minute measurement is now under study in order to evaluate the difference of dissolution rate between [P - 1] and [P]. Among three monomers or corresponding unit structures of them in polymer, chemical bonding structures around hydroxyl group are almost the same. It should be pointed out that the surroundings of hydroxyl group in each polymer are significantly different.

Insolubility to water is the essential character for 193nm immersion top coat because it is used in contact with immersion medium, purified water. All the polymers were of course insoluble to water as these were fluoropolymers which were generally

Table 2 Properties for Immersion Material.

	Abs. ^(a) at 193nm [μm^{-1}]	Dissolution character (to water)	Contact angle ^(b) [°]	Refractive index [-]	Extinction index [-]
[P - 1]	0.01	insoluble	81	1.46	1.17×10^{-3}
[P]	0.04	insoluble	70	1.48	2.46×10^{-3}
[P + 1]	0.04	insoluble	82	1.49	3.31×10^{-3}

(a) Absorption coefficient (b) against water

water repelling.

3.3.5 Refractive index and contact angle for 193nm top coat

Refractive indices were in the range from 1.45 to 1.50, a little below 1.56 that is most favorable value in the case of water as immersion medium⁽¹²⁾.

Water repellency is one of the required features for the material. To evaluate it, water contact angle to water was measured lastly (Table 2). Among three polymers, [P - 1] and [P + 1] possessed relatively high water repelling character. However, the contact angle of [P - 1] was changed with time, and indeed, got worse only after 10 seconds. The cause of this strange phenomenon is under study.

The refractive indices and contact angles of both [P - 1] and [P] are suitable for a top coat for immersion.

As described above, newly synthesized homopolymers [P - 1] and [P + 1] were found to have both advantages and disadvantages for application independently to a 157nm resist base polymer. However, those monomers can be used as comonomers. We are now studying copolymerization of [M - 1] with [M] and [M - 1] with [M + 1] in order to improve the weak points of [P - 1] and [P + 1]. Dissolution character of [P - 1] was excellent, and copolymer including the unit derived from [M - 1] must have a potential to improve the dissolution character of [P] or [P + 1].

4. Conclusion

We have synthesized two new partially fluorinated dienes, 1,1,2,3,3-Pentafluoro-4-trifluoromethyl-4-hydroxy-1,5-hexadiene [M - 1] and 1,1,2,3,3-Pentafluoro-4-trifluoromethyl-4-hydroxy-1,7-octadiene [M + 1]. These monomers were polymerized and physical properties of resulting polymers were investigated compared with FPR to apply to photoresists or something for 157nm and 193nm lithography. Revealed was the following.

1. Both two new monomers were easily polymerized under standard radical polymerization condition and gave solvent-soluble amorphous polymers that had cyclic

structures.

2. The polymer [P - 1] from [M - 1] possessed excellent solubility to standard developer, tetramethylammounium hydroxide aqueous solution, good transparency at 157nm wavelength, but too low Tg as a resist base polymer. It had optical character and solubility good enough for top coat material for 193nm immersion lithography.
3. The polymer [P] from [M] possessed good solubility to developer, excellent transparency at 193nm, and high heat resistance. This was a good candidate for top coat as well as [P - 1].
4. The polymer [P + 1] from [M + 1] possessed high Tg but inadequate solubility to developer as a resist base polymer.

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