Surface Grafting of Polymers onto Glass Plate: Polymerization of Vinyl Monomers Initiated by Initiating Groups Introduced onto the Surface

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ABSTRACT: The surface grafting of polymers onto a glass plate surface was achieved by the polymerization of vinyl monomers initiated by initiating groups introduced onto the surface. Azo groups were introduced onto the glass plate surface by the reaction of 4,4′-azobis(4-cyanopentanoic acid) with isocyanate groups, which were introduced by the treatment with tolylene-2,4-diisocyanate. The radical polymerization of various vinyl monomers was initiated by azo groups introduced onto the glass plate surface and the corresponding polymers were grafted from the surface: The surface grafting of polymers was confirmed by IR spectra, and the contact angle of surface, with water. The contact angle of the glass plate increased by the grafting of hydrophobic polymers, but decreased by the grafting of hydrophilic polymers. The radical postpolymerization was successfully initiated by the pendant peroxycarbonate groups of grafted polymer on the surface to give branched polymer-grafted glass plate. The cationic polymerization of vinyl monomers was also successfully initiated by benzylium perchlorate groups introduced onto the glass plate surface and the corresponding polymers were grafted onto the surface. The contact angle of the glass plate surface obtained from the cationic polymerization of styrene was larger than that obtained from the radical polymerization. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65**: 2165–2172, 1997

Key words: glass plate; surface grafting of polymer; branched polymer; contact angle; azo group

INTRODUCTION

It has been reported that carboxyl and phenolic hydroxyl groups on carbon black and silanol groups on ultrafine silica undergo chemical reactions and they are readily converted to reactive functional groups.[1,2] For example, azo[3] and peroxyester,[4] potassium carboxylate,[5] and benzylium perchlorate groups[6] introduced onto an ultrafine silica surface have abilities to initiate the anionic, cationic, and radical graft polymerization, respectively. Polymer-grafted carbon black and silica with a high percentage of grafting is obtained from the above polymerization system, because the grafted chains are propagated from the surface-initiating groups.
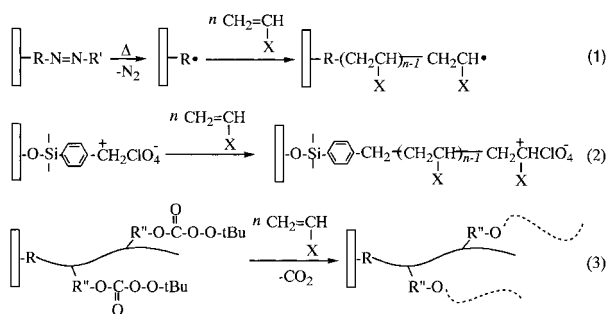
In addition, we have reported that the effective grafting of polymers onto the silica surface is achieved by the graft polymerization of various vinyl monomers initiated by radicals formed by the photodecomposition of azo groups introduced onto the surface.[7] More recently, the postgraft polymerization of vinyl monomers onto the silica surface has been reported to be successfully initiated by pendant peroxycarbonate groups of grafted polymer, such as poly-

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(methyl methacrylate-*co-tert*-butylperoxy-2-meth-acryloyloxyethylcarbonate), on the surface to give branched polymer-grafted silica with a high percentage of grafting.[8]

In a previous article, we reported the control of surface wettability of carbon thin film by the grafting of polymers initiated by azo, acylium perchlorate, and potassium carboxylate groups introduced onto the surface.[9] In this study, to modify the wettability of the glass plate surface, the grafting of polymers onto the surface by the polymerization initiated by azo [eq. (1)] and benzylium perchlorate groups [eq. (2)] was investigated. Furthermore, the postgraft polymerization of vinyl monomers initiated by pendant peroxycarbonate groups of grafted polymers onto the glass plate [eq. (3)] is discussed.

$$
\boxed{-R-N=N-R'} \xrightarrow[-N_2]{\Delta} \boxed{-R\bullet} \xrightarrow{n\ CH_2=CH \atop X} \boxed{-R-(CH_2CH)_{\overline{n-1}} CH_2CH\bullet \atop X \qquad X} \quad (1)
$$

$$
\boxed{-O-Si-\bigcirc-CH_2ClO_4^-} \xrightarrow{n\ CH_2=CH \atop X} \boxed{-O-Si-\bigcirc-CH_2(CH_2CH)_{\overline{n-1}} CH_2\overset{+}{C}HClO_4^- \atop X \qquad X} \quad (2)
$$

$$
\boxed{-R} \overset{R''-O-\overset{O}{\overset{\|}{C}}-O-O-tBu}{\underset{R''-O-\underset{\|}{\underset{O}{C}}-O-O-tBu}{\diagup\diagdown}} \xrightarrow[-CO_2]{n\ CH_2=CH \atop X} \boxed{-R} \overset{R''-O\diagdown}{\underset{R''-O\diagup}{\diagup\diagdown}} \quad (3)
$$

EXPERIMENTAL

Glass Plate

Glass plate ($10 \times 15 \times 1.0$ mm) was obtained from Iwaki Glass Co., which was washed with chloroform and treated with an HCl aqueous solution (1.0 mol/L) at 50°C for 8 h. The resulting glass plate was repeatedly washed with pure water and dried *in vacuo* at 110°C before use.

Monomers

Styrene was washed with a 5% aqueous solution of NaOH and water, dried over $CaCl_2$, and distilled twice under reduced pressure. *N*-Vinyl-2-pyrrolidone (NVPD) was dried over NaOH and distilled twice under reduced pressure. Methyl methacrylate (MMA) was washed with a 10% aqueous solution of $NaHSO_3$, a 5% aqueous solution of NaOH, and a 20% aqueous solution of NaCl. It was dried over anhydrous $NaSO_4$ and distilled twice under reduced pressure. *N*-Vinylcarbazole (NVC) was re-

crystallized from *n*-hexane. Acrylic acid (AA), perfluorohexylethyl acrylate (PFHEA) obtained from Hoechest Japan Ltd., and *tert*-butylperoxy-2-methacryloyloxyethylcarbonate (HEPO) obtained from Nippon Oil and Fats Co. were distilled under reduced pressure.

Reagents

Benzene and toluene were washed with concentrated H_2SO_4, a 5% aqueous solution of NaOH and water, and dried over $CaCl_2$, refluxed over sodium, and distilled. Nitrobenzene was washed with dilute H_2SO_4, dried over $CaCl_2$, and distilled. Dimethyl sulfoxide (DMSO) was dried over CaH_2 and distilled twice under reduced pressure. Tolylene-2,4-diisocyanate (TDI) was distilled just before use. 4,4′-Azobis(4-cyanopentanoic acid) (ACPA) obtained from Wako Pure Chemical Co. was recrystallized from methanol. 4-(Chloromethyl)-phenyltrimethoxysilane (CMTMS) obtained from Chisso Co., tetrahydrofuran (THF), and α-pycorin were used without further purification.

Introduction of Azo Groups onto Glass Plate

The introduction of azo groups onto the glass plate surface was achieved by the reaction of ACPA with isocyanate groups, which were introduced by the treatment with TDI. Glass plate ($10 \times 5 \times 1.0$ mm) was treated with an excess of TDI (5.0 mL) in DMSO (60 mL) at 60°C for 4 h. After cooling the reaction mixture to room temperature, ACPA (2.0 g) was added to the mixture and the reaction was continued at room temperature for 8 h. The resulting glass plate was repeatedly washed with methanol and dried *in vacuo* at room temperature. The glass plate having azo groups is abbreviated as GP-Azo.

Introduction of Benzylium Perchlorate Groups onto Glass Plate

The introduction of benzylium perchlorate groups onto the glass plate, i.e., pretreatment, was achieved by the reaction of silver perchlorate with surface benzyl chloride groups, which were introduced by the treatment with CMTMS.[6] The glass plate was treated with 5.0 mL of CMTMS in 150 mL of toluene at 110°C for 8 h. After the reaction, the glass plate was washed with absolute THF and dried *in vacuo*. The resulting glass plate was treated with 0.02 g of silver perchlorate in 10.0
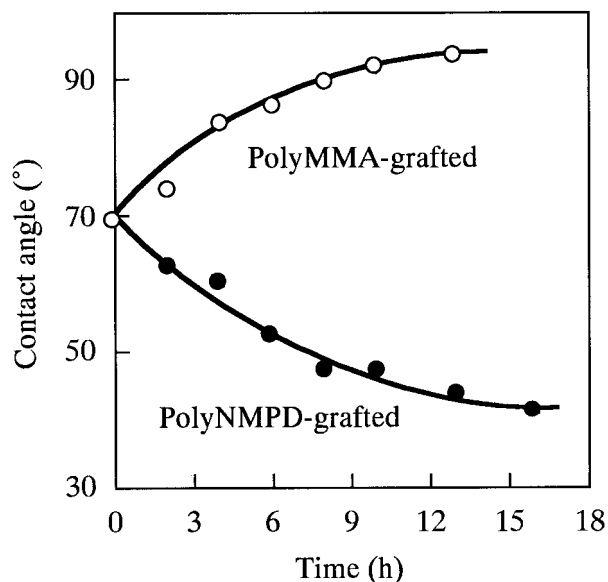
mL of nitrobenzene at room temperature for 48 h. The glass plate having benzyl chloride and benzylium perchlorate groups are abbreviated as GP-CH_2Cl and GP-$CH_2^+ClO_4^-$, respectively.

Radical Graft Polymerization Initiated by GP-Azo

Into a glass ampule that contained a stirrer bar, GP-Azo, the vinyl monomer, and the solvent were charged. The ampule was cooled by liquid nitrogen, thawed three times, and sealed *in vacuo.* The polymerization was carried out under stirring with a magnetic stirrer at 80°C. After the polymerization, the glass plate was washed with THF repeatedly and dried *in vacuo.*

Photopolymerization of Styrene Initiated by GP-Azo

Into a photoreactor (Riso-Kagaku Sangyo Co., Model UVL-100H), GP-Azo, 30.0 mL of styrene, and 10.0 mL of benzene as the solvent were added. The reaction mixture was irradiated with a 100 W high-pressure UV light under stirring with a magnetic stirrer at room temperature. After the polymerization, the glass plate was washed with THF repeatedly and dried *in vacuo.*

Cationic Graft Polymerization Initiated by GP-$CH_2^+ClO_4^-$

After the pretreatment for the introduction of benzylium perchlorate groups onto the glass plate surface, 10.0 mL of the monomer was added and the polymerization was conducted at 40°C under nitrogen. After the polymerization, the glass plate was washed with THF repeatedly and dried *in vacuo.*

Determination of Contact Angle of Glass Plate Surface with Water

The contact angle of the glass plate with pure water was determined by the method in the literature.[10]

IR Spectra of Polymer-grafted Glass Plate Surface

The IR spectra of polymer-grafted glass plate was recorded on a Shimadzu FT-IR spectrophotometer, Model DR-8020, using a multireflection method.

Table I Contact Angle of Polymer-grafted Glass Plate with Water

GP	Contact Angle (°)
Untreated	0–10
GP-Azo	70
Polystyrene-grafted[a]	92
PolyMMA-grafted[a]	90
PolyNVPD-grafted[b]	47
PolyNVC-grafted[c]	77
PolyPFHEA-grafted[d]	114

[a] Monomer, 15.0 mL; benzene, 5.0 mL; 80°C; 8 h.
[b] NVPD, 20.0 mL; 80°C; 8 h.
[c] NVC, 3.9 g; benzene, 20.0 mL; 80°C; 8 h.
[d] PFHEA, 5.0 mL; toluene, 10.0 mL; 80°C; 8 h.

RESULTS AND DISCUSSION

Introduction of Azo Groups onto Glass Plate

It has been reported that azo groups are introduced onto the ultrafine silica surface and the graft polymerization of vinyl monomers are initiated by the azo groups.[1-3] Therefore, the introduction of azo groups onto the glass plate surface by the reaction of ACPA with surface isocyanate groups, which were introduced onto the surface by the treatment with TDI [eq. (4)], was investigated.

Table I shows the contact angle of the glass plate with water after the treatment with TDI and ACPA. It was found that the contact angle of the surface was increased to 70° by the treatment of glass plate with TDI followed by ACPA. This result suggests that azo groups were introduced onto the glass plate surface. In the infrared spectra of the ACPA-treated plate surface, however, adsorptions which are characteristic of ACPA were hardly observed, because of the extremely low content of surface ACPA groups. The glass plate having azo groups is abbreviated as GP-Azo.

Radical Graft Polymerization Initiated by GP-Azo

The radical polymerization of styrene, MMA, NVPD, NVC, and PFHEA was carried out in the presence of GP-Azo. The results are also shown

Figure 1 Relationship between polymerization time and contact angle of glass plate with water in the radical grafting of polyMMA and polyNVPD. The polymerization conditions are given in Table I.

in Table I. The change of the contact angle of the glass plate before and after the polymerization in the presence of the untreated glass plate was scarcely observed. On the contrary, the contact angle of the glass plate obtained from the polymerization of styrene, MMA, NVC, and PFHEA in the presence of GP-Azo increased in comparison with that of GP-Azo and that of NVPD decreased. The contact angle of these polymer-grafted glass plates nearly reached those of the corresponding polymer films: For example, the contact angle of the glass plate obtained from the polymerization of styrene was nearly equal to that of the polystyrene film: 107°.[11]

Figure 1 shows the relationship between the polymerization time and the contact angle of the glass plate during the polymerization of MMA and NVPD in the presence of GP-Azo. The contact angle of the glass plate obtained from the polymerization of MMA in the presence of GP-Azo increased with progress of the polymerization. On the contrary, the contact angle of the glass plate surface obtained from the polymerization of hydrophilic NVPD decreased with the progress of the polymerization.

The contact angle of the polyMMA-grafted glass plate no longer increased after 8 h and that of the polyNVPD-grafted glass plate no longer decreased after 8 h. This indicates that at the last

stage of the polymerization the grafted polymer chains on the surface interfere with the approach of vinyl monomers to surface radicals formed by the decomposition of azo groups and also interfere with the propagation of polymers from neighboring azo groups.

In the infrared spectra of the polyMMA-grafted glass plate surface, new adsorptions at 1730 and 1129 cm^{-1}, which are characteristic of polyMMA, were observed. The film thickness, however, could not be determined.

Based on the above results, it is concluded that GP-Azo has the ability to initiate the radical graft polymerization of vinyl monomers and that grafted polymer chains are propagated from the surface radicals formed by the thermal decomposition of azo groups on the surface.

Effect of Polymerization Temperature on the Grafting

It has been reported that in the radical polymerization of vinyl monomers initiated by initiating groups introduced onto silica the percentage of grafting and conversion are affected by the polymerization temperature.[12] Therefore, the effect of polymerization temperature on the graft polymerization of styrene initiated by GP-Azo was investigated. The results are shown in Table II. The contact angle of the glass plate surface increased with increasing polymerization temperature. This may be due to the effective formation of initiating radicals by the decomposition of surface azo groups at higher temperature.

Effect of Polymerization Solvent on the Grafting

The effect of solvent on the radical polymerization of styrene initiated by GP-Azo was investigated: In this study, the solvent used as a good solvent was benzene and that used as a poor solvent was

Table II   Effect of Polymerization Temperature on the Grafting of Polystyrene onto Glass Plate Surface

Temperature (°C)	Contact Angle (°)
40	76
60	85
80	92

Styrene, 15.0 mL; benzene, 5.0 mL; 8 h.

Table III   Effect of Polymerization Solvent on the Grafting of Polystyrene onto Glass Plate Surface

Solvent	Contact Angle (°)
Water	76
Methanol	84
Benzene	92

Styrene, 15.0 mL; solvent, 5.0 mL; 80°C; 8 h.

water and methanol. The results are shown in Table III. The contact angle of the glass plate surface obtained from polymerization in the poor solvent were smaller than that obtained from polymerization in the good solvent. This indicates that the propagation of grafted polymer chains are inhibited in the poor solvent, because polystyrene chains became a random coil formation.

Photopolymerization Initiated by GP-Azo

The graft polymerization initiated by surface radicals formed by the photodecomposition of azo groups introduced onto the glass plate surface was investigated at room temperature. The results are shown in Table IV. The contact angle of the glass plate increased after the polymerization of the hydrophobic monomer in the presence of GP-Azo, but decreased after the polymerization of the hydrophilic monomer: The contact angle of the polystyrene-grafted glass plate increased from 70° to 99°. However, in the presence of the untreated glass plate, no grafting of polymers onto the surface was observed. Based on the above results, it was concluded that the photopolymerization of vinyl monomers is initiated by the azo groups in-

Table IV   Grafting of Polymers onto Glass Plate Surface by Photopolymerization Initiated by GP-Azo

GP	Contact Angle (°)
Untreated	0–10
GP-Azo	70
Polystyrene-grafted	99
PolyMMA-grafted	92
PolyNVPD-grafted	44
PolyAA-grafted	54

Monomer, 30.0 mL; benzene, 10.0 mL; 25°C; 8 h.
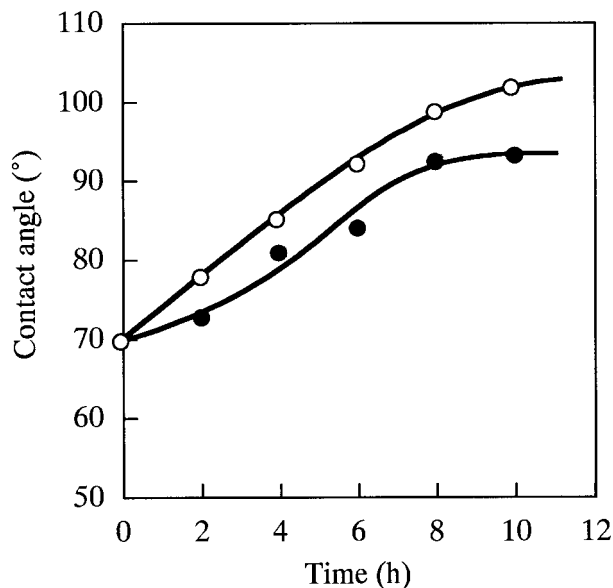
Figure 2   Relationship between polymerization time and contact angle of glass plate with water in the thermal polymerization and photopolymerization of styrene initiated by GP-Azo: (○) photopolymerization at room temperature; (●) thermal polymerization at 80°C.

troduced onto the glass plate surface and the corresponding polymers are grafted onto the surface.

The contact angle of the glass plate surface obtained from the polymerization of styrene initiated by the photodecomposition of azo groups, i.e., photopolymerization, was compared with that from the polymerization initiated by the thermal decomposition of the azo groups, i.e., thermal polymerization. Figure 2 shows the relationship between polymerization time and contact angle during the thermal and photopolymerization of styrene initiated by GP-Azo.

It is interesting to note that the contact angle of the glass plate surface obtained from the photopolymerization was higher than that obtained from the thermal polymerization. The same tendency was observed in the thermal polymerization and photopolymerization initiated by azo groups introduced onto silica and the carbon thin-film surface.[7,9] These results are explained as follows: In the thermal polymerization, since the decomposition of the surface azo groups is considered to proceed gradually, the grafted polymer chains on the surface interfere with the propagation of polymers from neighboring azo groups [eq. 5(a)]. On the contrary, in the photopolymerization, the decomposition of the surface azo groups is considered to proceed simultaneously. Therefore, the

propagation of polymer chains proceed effectively, because shielding of the surface radical was reduced [eq. 5(b)].

(a) Thermal Polymerization

(5a)

(b) Photopolymerization

(5b)
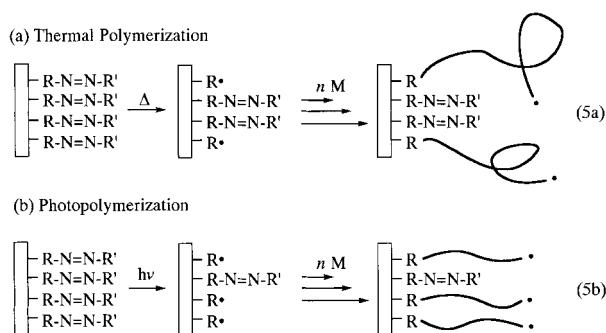
In other words, the initiator efficiency in the photopolymerization is higher than that in the thermal polymerization.

Postpolymerization Initiated by Pendant Peroxycarbonate Groups of Surface-grafted Polymer Chain

It has been reported that the radical postpolymerization of vinyl monomers is initiated by grafted poly(MMA-*co*-HEPO) onto silica to give a branched polymer-grafted silica with a high percentage of grafting.[8] Therefore, the grafting of polymers having pendant peroxycarbonate groups onto the glass plate surface was achieved by the copolymerization of MMA with HEPO initiated by surface azo groups introduced onto the surface at 80°C. At that temperature, the decomposition of pendant peroxycarbonate groups is reported to be considerably small.[13]

Table V shows the results of the copolymerization of HEPO with MMA initiated by azo groups introduced onto the glass plate surface. The contact angle of the poly(MMA-*co*-HEPO)-grafted glass plate decreased with increasing HEPO content of the grafted copolymer. This may be due to the hydrophilic nature of HEPO moieties in poly(MMA-*co*-HEPO).

The postpolymerization of PFHEA was carried out in the presence of the poly(MMA-*co*-HEPO)-grafted glass plate at 100°C. The results are also shown in Table V. The contact angle of the glass plate obtained after the postpolymerization of PFHEA in the presence of the poly(MMA-*co*-HEPO)-grafted glass plate was increased: The contact angle of the glass plate surface obtained from the postpolymerization was nearly equal to

that of the polytetrafluoroethylene film. This indicates that the postpolymerization of PFHEA is successfully initiated by pendant peroxyester groups of grafted poly(MMA-*co*-HEPO) onto a glass plate and branched polymer is grafted onto the surface. Furthermore, the contact angle of the glass plate after postpolymerization of PFHEA increased with increase of the HEPO content in the grafted copolymer. This may be due to the increase of the content of pendant peroxycarbonate groups of grafted poly(MMA-*co*-HEPO).

Cationic Graft Polymerization Initiated by GP-CH$_2^+$ClO$_4^-$

It has been reported that surface benzylium perchlorate groups introduced onto ultrafine silica have the ability to initiate the cationic graft polymerization of various monomers to give the corresponding polymer-grafted silica.[6] Therefore, the cationic graft polymerization of vinyl monomers initiated by surface benzylium perchlorate groups, which were introduced onto the glass plate surface by the reaction of silver perchlorate with surface benzyl chloride groups, was investigated [eq. (6)].
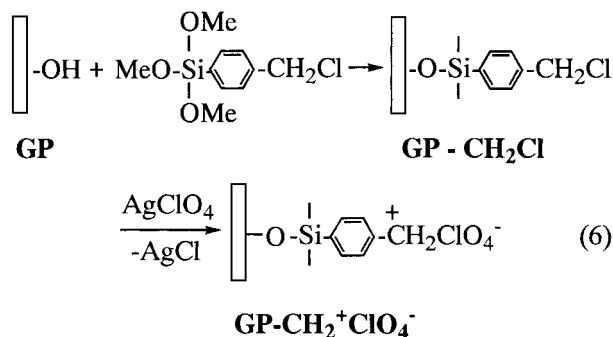

(6)

Figure 3 shows the relationship between the polymerization time and contact angle of glass plate surface obtained from the cationic polymerization of styrene and NVPD. It was found that the contact angle of the glass plate during the polymerization of styrene increased with the progress of the polymerization, but decreased during the polymerization of NVPD.

Table VI shows the results of the cationic graft polymerization of vinyl monomers initiated by GP-CH$_2^+$ClO$_4^-$. It was found that surface benzylium perchlorate groups have abilities to initiate the cationic polymerization of vinyl monomers to give the corresponding polymer-grafted glass

Table V   Contact Angle of Poly(MMA-*co*-HEPO)-grafted and PolyPFHEA-postgrafted Glass Plate

Molar Ratio in Feed (MMA : HEPO)	Contact Angle (°)	
	Poly(MMA-*co*-HEPO)-grafted	PolyPFHEA-postgrafted
0.70 : 0.30	63	114
0.80 : 0.20	62	110
0.90 : 0.10	68	105

plate: The glass plate surface shows a hydrophilic nature by the grafting of hydrophilic polymers, but shows a hydrophobic nature by the grafting of hydrophobic polymers.

It has been reported that the molecular weight of polystyrene grafted onto silica obtained from the radical graft polymerization initiated by surface azo groups is much larger than that obtained from the cationic polymerization. The number of grafted polystyrene in the radical polymerization, however, was much less than that in the cationic polymerization.[14] In addition, it has been reported that the contact angle of polystyrene-grafted carbon film obtained from the cationic graft polymerization is larger than that obtained from radical graft polymerization.[9] Therefore, the contact angle of the glass plate obtained from the cationic polymerization initiated by benzylium perchlo-

rate groups on the surface was compared with that obtained from the radical polymerization initiated by azo groups on the surface (Fig. 4).

As shown in Figure 4, in both systems, the contact angle increased with the progress of the polymerization. The contact angle of the glass plate surface obtained from the cationic polymerization was higher than that obtained from the radical polymerization. This may be due to the difference in the grafted polymer chain length and the number of grafted chains between the cationic and radical initiation systems. Further detailed analysis on the polymer film thickness on the glass plate obtained from the cationic and radical polymerization systems is now under investigation.

CONCLUSIONS

1. Azo groups were introduced onto the glass plate surface by the reaction of ACPA with isocyanate groups, which were introduced by the treatment with TDI. The graft polymerization of various vinyl monomers were initiated by the thermal decomposition and photodecomposition of surface azo groups
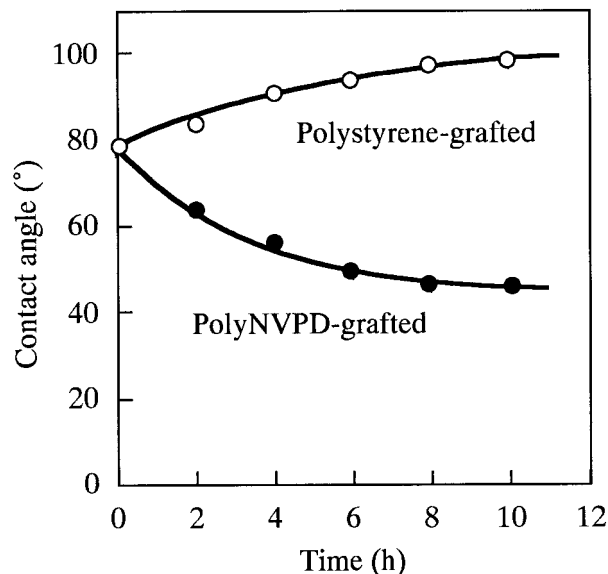

Figure 3   Relationship between polymerization time and contact angle of glass plate with water in the cationic grafting of polystyrene and polyNVPD. The polymerization conditions are given in Table VI.

Table VI   Contact Angle of Polymer-grafted Glass Plate by Cationic Polymerization Initiated by GP-CH$_2^+$ClO$_4^-$

GP	Contact Angle (°)
Untreated	0–10
GP-CH$_2$Cl	78
Polystyrene-grafted[a]	98
PolyNVPD-grafted[a]	46
PolyNVC-grafted[b]	79

[a] Monomer, 10.0 mL; nitrobenzene, 10.0 mL; 40°C; 8 h.
[b] NVC, 3.9 g; benzene, 10.0 mL; nitrobenzene, 10.0 mL; 40°C; 8 h.
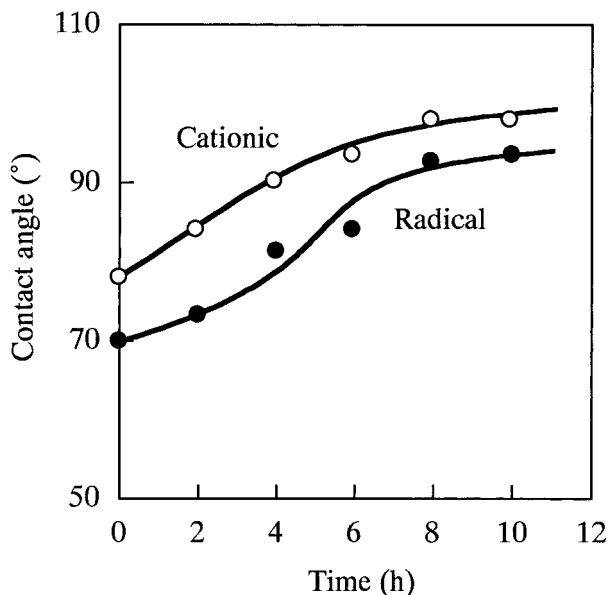
Figure 4   Contact angle of polystyrene-grafted glass plate with water in the radical and cationic polymerization.

and the corresponding polymers were grafted onto the surface.

2. The postpolymerization of PFHEA was successfully initiated by pendant peroxycarbonate groups of grafted poly(MMA-*co*-HEPO) onto the glass plate surface and the branched polymer was grafted onto the surface.

3. Benzylium perchlorate groups were introduced onto the glass plate surface by the reaction of silver perchlorate with benzyl chloride groups introduced onto the glass plate surface. The cationic polymerization of vinyl monomers was initiated by the benzyl-ium perchlorate groups. The contact angle of the glass plate surface obtained from the cationic polymerization was larger than that obtained from the radical polymerization.

4. The wettability of the glass plate surface was controlled by the grafting of polymers onto the surface: The glass plate surface showed a hydrophilic nature by the grafting of the hydrophilic polymer, but showed a hydrophobic nature by the grafting of the hydrophobic polymer.

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