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Synthesis of fluorine-containing graft copolymers of poly(perfluoroalkylethyl methacrylate)-*g*-poly(methyl methacrylate) by the macromonomer technique and emulsion copolymerization method

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A new method of synthesizing graft copolymers having a poly(perfluoroalkylethyl methacrylate) (PFMA) backbone has been suggested and illustrated by preparing poly(perfluoroalkylethyl methacrylate)-*g*-poly(methyl methacrylate)s (PFMA-*g*-PMMA). These copolymers were prepared using the macromonomer technique and emulsion copolymerization method. PMMA macromonomers were synthesized by acylation of hydroxyl-group terminated PMMAs which were prepared by radical oligomerization of methyl methacrylate with a chain-transfer agent. The PMMA macromonomer was copolymerized with a comonomer of perfluoroalkylethyl methacrylate (FMA) by emulsion polymerization to obtain graft copolymers of PFMA-*g*-PMMA. Toluene was chosen as a suitable solvent to obtain stable emulsions containing PMMA macromonomer and FMA for copolymerization. Graft copolymers having various PMMA compositions and branch lengths could be prepared. It is confirmed that the desired graft copolymers were successfully prepared and that the method suggested for synthesizing PFMA-*g*-PMMAs is useful in the manufacture of various surface modification agents. © 1997 Elsevier Science Ltd.

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INTRODUCTION

Heterogeneous (two-phase) graft copolymers tend to show the properties of the components rather than an averaging of homopolymer properties. Not only do graft copolymers have properties different from those of homopolymers, random copolymers and polyblends, but the properties of graft copolymers themselves differ depending upon the compositions and arrangement of the segment homopolymers. A two-phase graft copolymer is expected to contain the merit of good miscibility with each homopolymer and have a desirable property of residing at the interface of the two phases. Therefore graft copolymers have attracted particular attention in the field of surface modification of various polymers and that of enhancing the miscibility of immiscible homopolymer phases[1,2].

Fluorine-containing graft copolymers having suitable miscibility for the surfaces to be treated have important applications as additives for modifying surface properties in the fields of coatings, adhesives, films, fibres and mouldings, because of their miscibility and extremely low surface energy. Random copolymers containing fluoropolymers are more widely used than graft copolymers as surface modification agents at present because there are many difficulties in preparing well-defined graft copolymers exhibiting both good miscibility and excellent surface properties.

A useful method for synthesizing graft copolymers is the macromonomer technique. A macromonomer is an oligomer with an end group that can copolymerize with comonomers to form comb-type graft copolymers. It can be prepared by ionic and free radical polymerization[3–6]. The resulting macromonomer can be copolymerized with a backbone-forming comonomer using free radical, cationic, anionic or insertion polymerization methods.

In this study, we suggest a valuable method for preparing fluorine-containing graft copolymers. Perfluoroalkylethyl methacrylate (FMA) was chosen as a fluorine-containing comonomer because its homopolymer (PFMA) exhibits extremely low surface energy[7,8] and has a wide range of applications as a surface modification agent[9,10]. Methyl methacrylate (MMA) was used for preparing the macromonomer. The fluorine-containing graft copolymers of poly(perfluoroalkylethyl methacrylate)-*g*-poly(methyl methacrylate) (PFMA-*g*-PMMA) were synthesized by emulsion copolymerization of PMMA macromonomer and FMA comonomer.

EXPERIMENTAL

Reagents

Methyl methacrylate (Junsei) and perfluoroalkylethyl

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methacrylate [$F(CF_2)_6CH_2CH_2COOCCH_3{=}CH_2$] (Hoechst, Fluowet MAE 600) were purified by distillation. The initiator, 2,2′-azobisisobutyronitrile (AIBN), was used for the preparation of macromonomers after recrystallizing three times from methanol. All the solvents used in this study, such as tetrahydrofuran (THF), chloroform, toluene, α,α,α-trifluorotoluene (TFT) and 1,1,2-trichlorotrifluoroethane (R-113), were spectrophotometric grade. Thioglycol (TG), acryloyl chloride (AC) and triethylamine (TEA) were reagent grade. The initiator 2,2′-azobis(2-amidinopropane) dihydrochloride (V-50) and nonionic surfactant polyoxyethylenenonylphenylether (average no. of ethylene oxide per mole = 50) (NP-50) were used directly as received for emulsion polymerization. Deionized water was used throughout the experiments.

Macromonomer synthesis

PMMA macromonomers having an acryloxy functional group at one end were synthesized by acylation of hydroxyl-group terminated PMMAs (HTPMMAs)[5] with AC as the following reaction scheme.

$$I \rightarrow R\cdot \quad (I{=}AIBN)$$

$$R\cdot + \underset{(TG)}{HOCH_2CH_2SH} \rightarrow HOCH_2CH_2S\cdot + RH$$

$$HOCH_2CH_2S\cdot + nM \rightarrow HOCH_2CH_2SM_n\cdot$$

$$HOCH_2CH_2SM_n\cdot + HOCH_2CH_2SH \rightarrow HOCH_2CH_2SM_nH + HOCH_2CH_2S\cdot \quad (HTPMMA)$$

$$HOCH_2CH_2SM_nH + \underset{(AC)}{CH_2{=}CHCOCl} \rightarrow CH_2{=}CHCOOCH_2CH_2SM_nH + HCl$$

(PMMA macromonomer)

The reaction was carried out as follows. AIBN, TG, THF and a magnetic stirrbar were introduced into a Pyrex vial. After purging with nitrogen, the vial was equipped with a Teflon-coated septum and pressurized to ca. 7 psig using nitrogen. The reaction was performed at 60°C and the conversions were detected by analysing the unreacted MMA with gas chromatography (g.c.). The reaction was terminated at conversion of about 40% by adding the reaction mixture into *n*-hexane. Purified HTPMMA was obtained after reprecipitating from *n*-hexane and drying in a vacuum oven. Acylation of HTPMMA was done by dropping 10% excess of AC on to the HTPMMA solution (HTPMMA/THF=1/2, w/w) for 30 min and ageing for 24 h at room temperature. The reaction solution was precipitated in *n*-hexane after neutralization with TEA and filtration with Celite. Purified PMMA macromonomer was obtained by reprecipitating and drying at room temperature. The molecular weights of HTPMMA and PMMA macromonomer were analysed by gel permeation chromatography (g.p.c.) (Waters R-401 ALC/GPC). The end-group functionality of the macromonomer was analysed by ^{1}H-n.m.r. (Bruker AMX 500) and g.p.c.

Graft copolymer synthesis

PFMA-*g*-PMMA was prepared by emulsion polymerization. The stable emulsions for the copolymerizations were obtained by adding organic solutions of toluene containing PMMA macromonomer and FMA (monomers/toluene = 1/1, w/w) dropwise to aqueous solutions containing a nonionic surfactant, NP-50 (NP-50/monomers = 0.05/1, w/w), and mixing simultaneously with a mechanical two-blade homomixer (IKA Labortechnik, T25). The content of the monomers in all the emulsions prepared was fixed to 20 wt%. After degassing, the emulsion copolymerization was done at 70°C for 6 h using an initiator, V-50 (V-50/FMA = 0.003/1, w/w), under ca. 7 psig nitrogen atmosphere. The graft copolymer was obtained as a precipitate by adding the reaction mixture dropwise to excess methanol and drying in a vacuum oven. It was then followed by extensive extraction with hot methanol using Soxhlet for 48 h to remove the unreacted monomers and surfactant.

Conversions of the macromonomer and FMA during the emulsion polymerization were measured by g.c. and liquid chromatography (l.c.), respectively. At the end of the reaction, the resulting conversions of the macromonomer and FMA were found to be ca. 70–80% and ca. 90%, respectively, for most of the copolymerizations. The structure and compositions of the segment homopolymers and the types of graft copolymer prepared were examined by *FT*-i.r. (Bio-rad FTS-40), ^{1}H-n.m.r. (Bruker AMX 500) and differential scanning calorimetry (d.s.c.) (DuPont 2100).

Synthesis of homopolymers and random copolymer

PFMA, PMMA and a random copolymer containing 52 wt% of FMA and 48 wt% of MMA were synthesized by radical polymerization. All the reactions were done using, as an initiator, 0.5 mol% of AIBN (based on the monomer) in a solvent of R-113/TFT mixture (30/70, w/w). The content of the monomer in the reaction mixture was 20 wt%. After degassing the reaction solution, polymerization was carried out at 70°C under ca. 7 psig nitrogen atmosphere for 24 h. PFMA, PMMA and the random copolymer were obtained as solids after precipitating three times from methanol and drying in a vacuum oven for 24 h.

RESULTS AND DISCUSSION

The preparation of PMMA macromonomer having controlled molecular weight, as illustrated in the reaction scheme described above, is an important first step in the preparation of the graft copolymers. Prior to obtaining the PMMA macromonomer, HTPMMA, which has a hydroxyl group (–OH) at one end, was prepared using TG as a chain transfer agent. *Figure 1* represents the relationship between the degree of polymerization (DP_n) of HTPMMA and the concentration ratio of TG to MMA ([TG]/[MMA]). It can be found that $1/DP_n$ of HTPMMA varies linearly according to the ratio [TG]/[MMA], which is in accordance with the results of Akemi *et al*[5]. By varying the ratio [TG]/[MMA], the molecular weight of HTPMMA can be controlled.

PMMA macromonomers having an acryloxy group at one end were prepared by acylation of HTPMMA with AC. The number-average molecular weights (M_n) of the PMMA macromonomers were characterized by g.p.c. and ^{1}H-n.m.r., and are summarized in *Table 1*, which shows an excellent coincidence between the results of g.p.c and ^{1}H-n.m.r. The end-group functionality of PFMA macromonomer was determined by ^{1}H-n.m.r. (*Figure 2A*). The acryloxy group content of the macromonomer can be calculated by the integral ratio

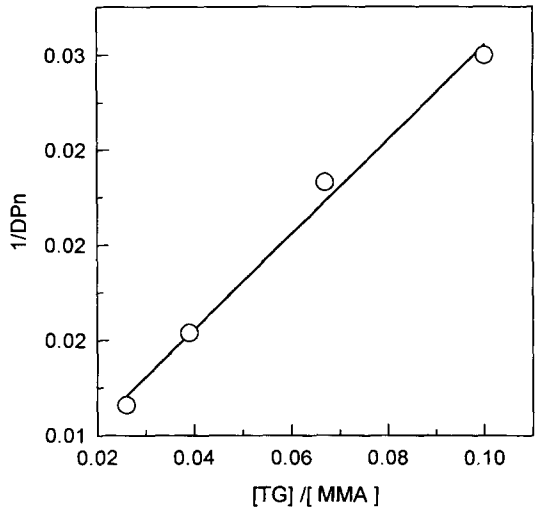

Figure 1 Variation of $1/DP_n$ of HTPMMA with ratio [TG]/[MMA]

Table 1 Comparison of number-average molecular weights of PMMA macromonomers measured by g.p.c. and ^{1}H-n.m.r.

	M_n (g mol^{-1})	
Sample no. of PMMA macromonomer	g.p.c.	^{1}H-n.m.r.
9K	9100	9200
3K	3250	3200

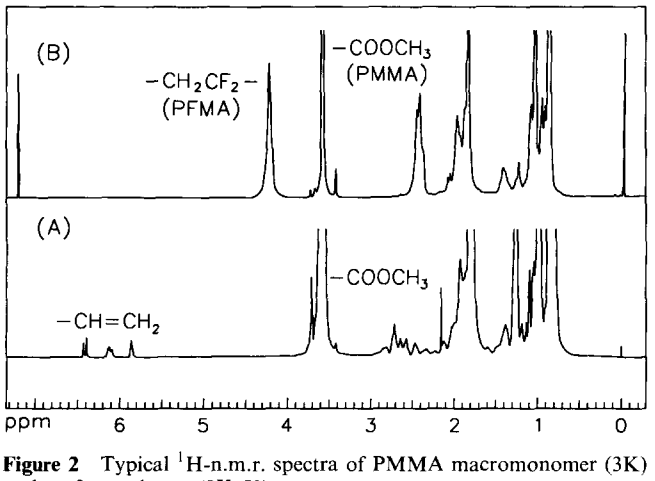

Figure 2 Typical ^{1}H-n.m.r. spectra of PMMA macromonomer (3K) and graft copolymer (9K-50)

Table 2 Comparison of compositions of PMMA macromonomer incorporated into graft copolymers with those initially charged to the reactions

	Composition of PMMA macromonomer (wt%)	
Sample no. of PFMA-*g*-PMMA	initially charged to the reaction	incorporated into the graft polymer
9K-30	30	10
9K-50	50	27
9K-70	70	57
3K-70	70	64

of acryloxy protons ($-COOCH=CH_2$, 5.8–6.5 ppm) to methyl protons ($-COOCH_3$, 3.6 ppm). From these results, it can be confirmed that an acryloxy group having a reactive double bond exists on the macromonomer molecule and that the acylation reaction to obtain the desired PMMA macromonomer was successfully achieved.

The PMMA macromonomers having an acryloxy group at one end were copolymerized with a backbone-forming comonomer of FMA by emulsion polymerization to obtain comb-type graft copolymers of PFMA-*g*-PMMA. It is very important to obtain stable emulsions containing the macromonomer and comonomers for emulsion graft copolymerization. The stable emulsions were obtained by using toluene as a dissolving agent for the PMMA macromonomers, which are solid at room temperature. Toluene is a good solvent for PMMA macromonomers, and has a low vapour pressure for fairly high reaction temperatures. Toluene was proven to be a suitable solvent that can make the emulsion of the reaction mixture highly stable throughout the polymerization reaction without phase separation.

A typical result of ^{1}H-n.m.r. analysis for the graft copolymers prepared in this study is shown in *Figure 2B*, where the peaks of $-CH_2CF_2-$ (4.3 ppm) and $-COOCH_3$ (3.6 ppm), originating from FMA and PMMA macromonomer respectively, can be found as indicated. This confirms that the graft copolymer containing FMA and PMMA macromonomer was successfully synthesized. The contents of PMMA macromonomer and FMA contained in the graft copolymers prepared can be calculated from the integral ratio of methyl protons ($-COOCH_3$) and methylene protons ($-COOCH_2-$) originating from PMMA and PFMA respectively[11].

In *Table 2* the contents of PMMA macromonomer calculated from the results of ^{1}H-n.m.r. analysis are compared with those initially fed to the reaction of the graft copolymerization. The graft copolymers of sample numbers 9K-30, 9K-50 and 9K-70 were prepared from the PMMA macromonomer having a molecular weight of about 9000 g mol^{-1}, and that of sample number 3K-70 from the PMMA macromonomer having a molecular weight of about 3000 g mol^{-1}. All the molecular weights of the graft copolymers in *Table 2* were measured to be above 100 000 g mol^{-1}. It can be observed that the content of PMMA macromonomer incorporated into the graft copolymers increases abruptly with increasing concentration of PMMA macromonomer initially charged to the reaction. Also, the graft copolymer prepared from the PMMA macromonomer having a lower molecular weight has a higher content of macromonomer for its same feed concentration, as can be seen by comparing the samples 9K-70 and 3K-70. This indicates that the PMMA macromonomer obtained has a reactive functionality, and that graft copolymers having various compositions of FMA and branch lengths of PMMA macromonomer can be synthesized. By comparing the graft copolymer 9K-70 with 3K-70, it can be also deduced that the reactivity of the acryloxy group of PMMA macromonomer depends upon its molecular weight, and that the macromonomer having the higher molecular weight has lower reactivity. This may be due to the steric hindrance of the branched side-chain of PMMA in the macromonomer[12].

Synthesis of the graft copolymers can also be confirmed by the analysis of *FT*i.r. and d.s.c. *Figure 3* shows the comparative results of *FT*i.r. analysis for the graft copolymer synthesized and PFMA homopolymer. The *FT*i.r. spectrum of PFMA homopolymer shows the C–F stretch observed at 1100–1200 cm^{-1}, but no C–H stretch is observed at 3000 cm^{-1}. On the other hand, both C–H and C–F stretches, which may originate from PMMA macromonomer and FMA monomer, are

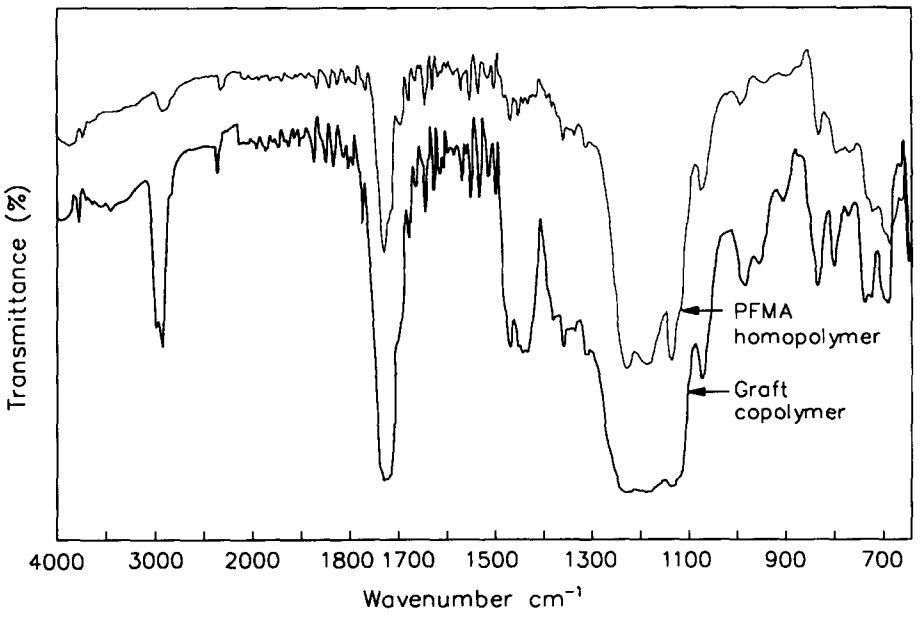

Figure 3 Comparison of *FT*i.r. spectrum of graft copolymer (9K-50) with that of PFMA homopolymer

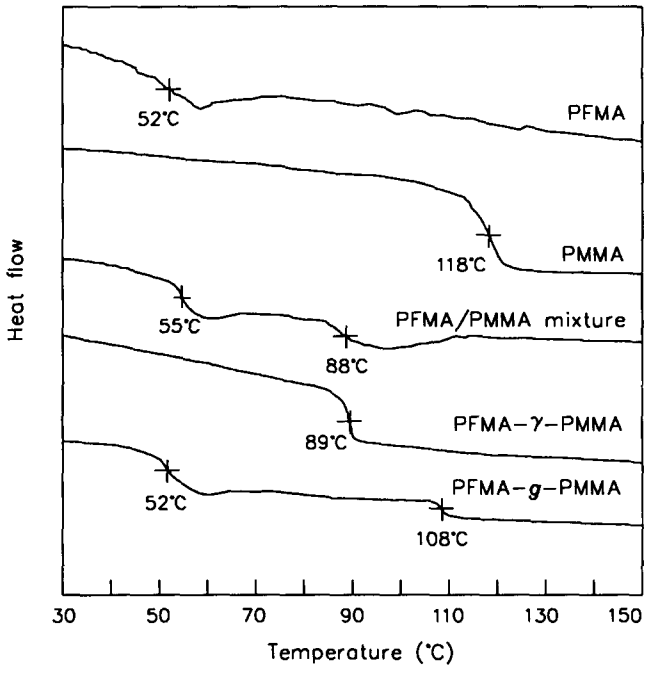

Figure 4 Comparison of glass transition temperatures between homopolymers of PFMA and PMMA, PFMA/PMMA (10/90, w/w) mixtures, random copolymer and graft copolymer (9K-30)

observed at 3000 cm^{-1} and 1100–1200 cm^{-1}, respectively, for the graft copolymer. This indicates that the graft copolymer has segments of both PMMA macromonomer and homopolymer of FMA.

To discriminate the graft copolymer and homopolymer blends, which could be synthesized by erroneous reaction, d.s.c. was carried out according to polymeric system. *Figure 4* shows a comparison of d.s.c. thermograms for homopolymers of PFMA and PMMA, PFMA/PMMA mixture (10/90, w/w), random copolymer and graft copolymer. The glass transition temperatures (T_gs) of the PFMA and PMMA homopolymers were found to be 52°C and 118°C, respectively. The homopolymer mixture (PFMA/PMMA) was observed to have two T_gs of 55°C and 88°C. The lower T_g may be due to a PFMA-rich phase in the PFMA/PMMA mixture, and the higher T_g due to a PMMA-rich phase. It seems that the PFMA/PMMA mixture has two phases, indicating that the two homopolymers of PFMA and PMMA are nearly immiscible. The random copolymer shows one T_g of 89°C that is placed between the T_gs of the homopolymers. This shows that the random copolymer has a third thermal property different from each segment homopolymer. On the other hand, the graft copolymer shows two T_gs of 52°C and 108°C, both nearly the same as those of the segment homopolymers. The higher T_g is slightly lower than that of the PMMA homopolymer (118°C). This may be because the segment homopolymer of PMMA macromonomer has relatively lower molecular weight than the PMMA homopolymer. The results of d.s.c. analysis strongly confirm the successful synthesis of a graft copolymer having a sufficiently large molecular weight.

Free-radical solvent copolymerizations were tried in order to obtain the graft copolymer using various solvents such as THF, TFT, R-113, chloroform, and mixtures of the previous solvents. Chloroform and R-113 are good solvents for homopolymers of PMMA and PFMA respectively. But it was difficult to choose a suitable solvent in which the graft copolymer is completely soluble. Because of the insufficient solubility of the graft copolymer, macrophase separation of the reaction mixture took place during the solvent graft copolymerizations and a low conversion of below ca. 20% was obtained even for an extremely low concentration of the monomers (about 5 wt%) in the reaction mixture and a long reaction time (7 days). It seems that a graft copolymer having a sufficiently high molecular weight cannot be prepared from PMMA macromonomer and FMA using the solvent polymerization method. That is, when the copolymerization is performed in a good solvent for PMMA macromonomer, the oligomeric graft copolymer of low molecular weight formed during the initial reaction is able to dissolve in the solvent. But, as the reaction proceeds, a graft copolymer of high molecular weight is formed, and the PFMA segment can no longer dissolve in the solvent. Phase separation occurs as a

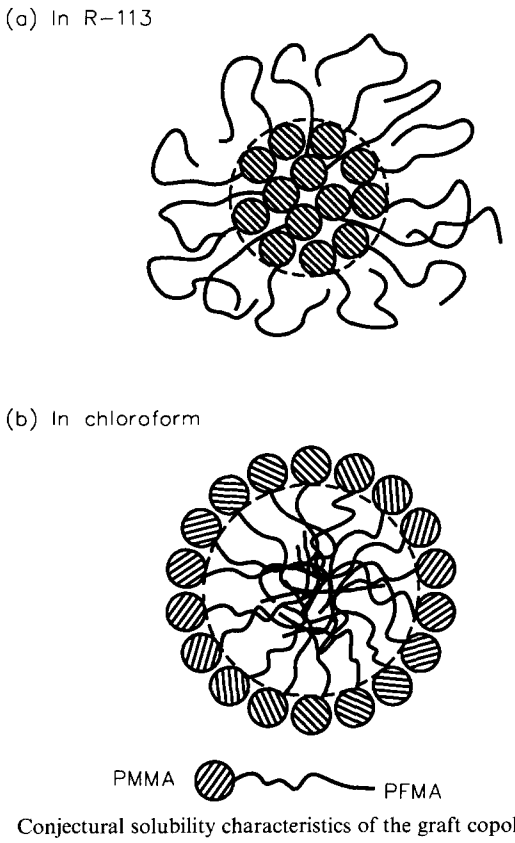

Figure 5 Conjectural solubility characteristics of the graft copolymer prepared

result and the reaction terminates. This is why the emulsion polymerization method was used to prepare the graft copolymer in this study.

To examine closely the phenomenon of macrophase separation during solvent copolymerization, the solubility characteristics of the graft copolymer synthesized were investigated. The graft copolymer dissolves in neither chloroform nor R-113, but shows a cloudy appearance of the colloidal state in either of these solvents. This is the solubility characteristic of two-phase heterogeneous graft copolymers[13]. *Figure 5* depicts the conjectural state of the graft copolymer in each solvent, which can explain the above solubility characteristics. It shows that the graft copolymer forms two opposite core-shell structures in each good solvent. This solubility characteristic also explains the vulnerable point of solvent copolymerization and the advantage of emulsion copolymerization for manufacturing the graft copolymer.

In the literature[14–16], fluorine-containing graft copolymers composed of PMMA branches and a PMMA-co-poly(perfluoroalkylethyl acrylate) backbone that is soluble in common solvents like benzene can be found. However, graft copolymers, which have a PFMA backbone that is not soluble in common solvents and are prepared by the macromonomer technique and emulsion polymerization method used in this study, have not been reported. The method suggested for synthesizing fluorine-containing graft copolymers will be suitable for important utilization in industry for manufacturing surface modification agents, because it is possible to prepare various graft copolymers having both low surface energy and good miscibility for the surfaces to be treated. In general, two-phase graft copolymers show good miscibility for segment homopolymers. Graft copolymers having a PFMA backbone which exhibits extremely low surface energy can be designed to have good miscibility for the materials to be treated by choosing suitable monomers forming branch segments.

CONCLUSIONS

A method for synthesizing graft copolymers having PMMA branches and a PFMA backbone has been suggested. A PMMA macromonomer having an acryloxy functional group at one end was prepared, and was then copolymerized with FMA comonomer by the emulsion polymerization method to obtain the desired graft copolymers. By analysing the graft copolymers using g.p.c., *FT*i.r., ^{1}H-n.m.r. and d.s.c., it was confirmed that the desired graft copolymers can be successfully prepared and that the method is useful for synthesizing comb-type graft copolymers having various compositions of FMA and branch lengths of acrylate monomers.

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