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Synthesis and Application of Fluorine Containing Graftcopolymers

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Summary

Well-defined graftcopolymers were prepared by radical copolymerization of methyl methacrylate macromonomer with perfluoroalkyl acrylate. Contact angle of the solvent cast films of poly(methyl methacrylate) containing various amount of the graftcopolymer was measured against water droplet. Addition of 0.2 wt% of the graftcopolymer was sufficient to improve the polymer films to water repellent surfaces, while 10 wt% was necessary to modify the polymer surfaces to the same level of water repellency.

Introduction

Surface properties of polymers are known to be of considerable importance in applications such as coatings, adhesives, films, fibers and moldings. Among many surface modification techniques including chemical, UV and plasma treatments, surface accumulation of functional segments by using tailor made graftcopolymers appear to be most promising to obtain a controlled surface structure for any particular application (YAMASHITA). As an approach to design functional graftcopolymers suitable for surface accumulation, we chose macromonomer technique recently developed for the

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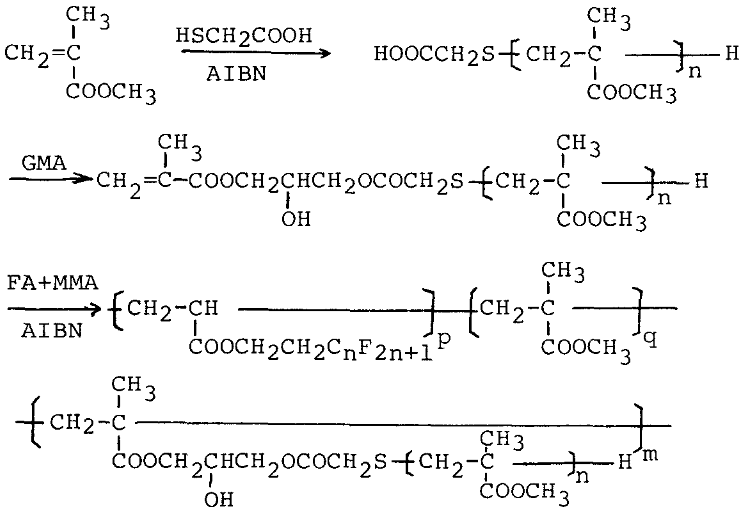
preparation of graftcopolymers of controlled architecture (WAITE, MILKOVICH). In a previous paper, we reported on the preparation of stearyl methacrylate-methyl methacrylate graftcopolymer and confirmed that the reactivity of the terminal double bond in the macromonomer is not different from conventional monomers in radical copolymerization (ITO et al). The present paper describes the preparation of methyl methacrylate (MMA)-perfluoroalkyl acrylate (FA) graftcopolymers and their application as surface modifier for poly MMA films.

Results and Discussion

Preparation of Graftcopolymers



The above scheme shows the preparation of the graftcopolymers by the macromonomer technique. MMA macromonomer with the molecular weight of about 3000 was synthesized by the polymerization of MMA in the presence of thioglycolic acid as a chain transfer agent to give MMA prepolymer having terminal carboxyl group, which was then reacted with glycidyl methacrylate to lead to terminal methacrylate group (ITO et al). The MMA macromonomer was copolymerized with appropriate mixture of MMA and FA to high conversion to the comb-type graftcopolymer. FA used was a commercial mixture of $CH_2=CHCOOCH_2CH_2C_nF_{2n+1}$ ($\bar{n}=6.0$), kindly supplied from Asahi Glass Co. The graftcopolymer was precipitated into methanol and purified by repeated extraction with methanol to remove unreacted macromonomer and oligomer. The molecular weight of the graftcopolymer was calculated from GPC by using calibration curve for polystyrene. Membrane osmometer was used to obtain the correct molecular weight for branched copolymers, but the results are not so much different from the GPC value, and the number of branches per polymer chain was between 4 and 8. The graftcopolymer is soluble both in fluorine containing solvent and ordinary solvent such as benzene or tetrahydrofuran and foaming solution is obtained characteristic for a surface active polymer. Table I gives the preparation and characterization of the graftcopolymers used in the present study together with a random copolymer for comparison.

TABLE I. Preparation of Graftcopolymers[a]

No.	feed PMMA macromonomer $\bar{M}_n(10^3)$	 wt%	 FA wt%	graftcopolymers Yield wt%	 FA[c] wt%	 $\bar{M}_n(10^3)$ GPC
GF-1	3.0	30.2	9	62.1	7.2	50
GF-2	3.0	29.6	21.6	64.8	18.3	50
GF-3	3.4	29.7	50.8	71.3	57.3	51
GF-4	3.0	50.0	50.0	70.6	57.7	79
RF-1	-	-	31.4	9.9[b]	51.0	-

[a] Copolymerization in $C_6H_5CF_3$ for 5 days, AIBN 1 mol% 60°C.

[b] Random copolymerization was stopped after 2 hrs.

[c] From C%

Contact angle of cast PMMA film containing graftcopolymers

PMMA films containing various amount of the graftcopolymer were cast from benzene solution onto clean glass slides. PMMA samples ($\overline{M_n}$ 1.0×10^5 and 1.6×10^5) were prepared by radical polymerization to low conversion, and purified by reprecipitation and freeze dried from benzene. Contact angles of droplets of water and dodecane were measured at 20°C using a sessile drop method. The results are shown in Figure 1 and 2. The shape of the curve is similar for the contact angle against water and dodecane, showing the similarity between water repellency and oil repellency by fluorocarbon segment. It seems that FA rich graftcopolymer is more effective for the modification of PMMA film surfaces, and addition of 0.2 wt% of the

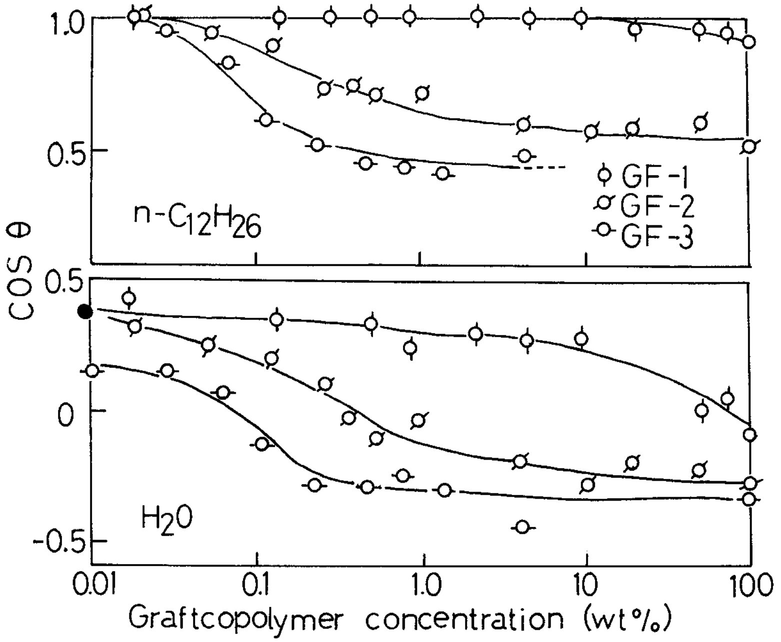


Figure 1 Contact angle of poly MMA cast films containing graftcopolymers, I

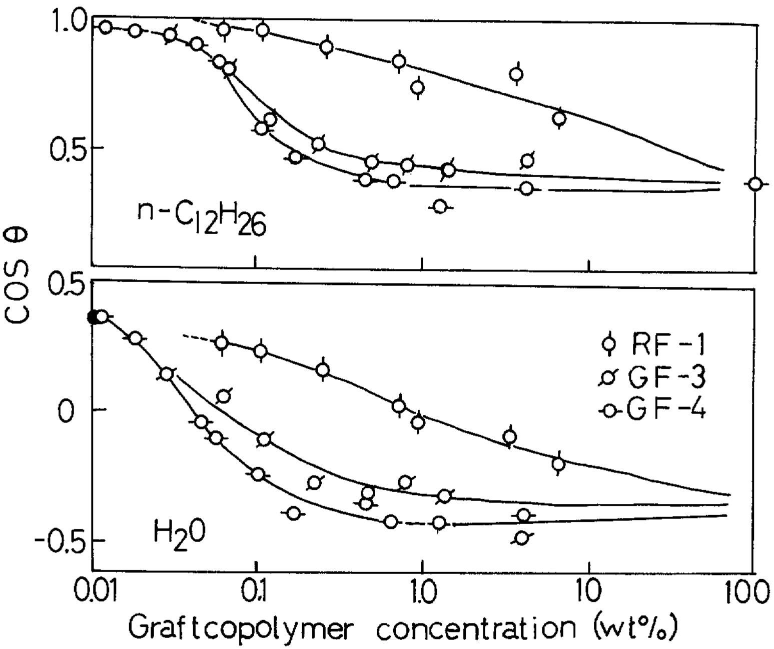


Figure 2 Contact angle of poly MMA cast films containing graftcopolymers, II

graftcopolymer containing 50 wt% of FA segment is sufficient to modify the PMMA surface to fluoropolymer like surfaces. Comparing the backbone structure of the graftcopolymer containing 50 wt% FA, FA homopolymer (GF-4) is slightly more effective than FA copolymer with MMA (GF-3). The great difference between random copolymer (RF-1) and graftcopolymer demonstrated the effect of the anchor segment, which might contribute to disperse the graftcopolymer in the PMMA matrix to form spherical domains suitable for surface accumulation of the fluorocarbon segment during solvent evaporation (GAINES Jr., G. L. and BENDER, G. W.). The anchor segment might be also effective to hold the low-energy FA surface for durable water repellency. Further studies seem necessary for the complete understanding of the situation.

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