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Alternating copolymerization of a surface-active monomer having an active ester group with dialkyl fumarates

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Radical homopolymerization of a cationic surface-active monomer bearing an active ester group, *p*-10-undecenoyloxyphenyldimethylsulfonium methylsulfate (UPDS) and its copolymerization with dialkyl fumarates (DRFs) were studied in water, benzene and dioxane as solvents, which give aqueous micellar, reverse micellar and isotropic solutions, respectively. The homopolymerization occurred only with 2,2′-azobis(2-amidinopropane) dihydrochloride (AIBA) in aqueous micellar solution, giving a polymer with a degree of polymerization of 14 and a narrow polydispersity ($\bar{M}_W/\bar{M}_n = 1.18$). Alternating copolymers of UPDS and DRFs with relatively high molecular weights were obtained in high yield, particularly in the copolymerizations of UPDS with DRFs in aqueous micellar solution using AIBA as a water soluble initiator. The depression of the rate of termination of the polymerization by the micelles was deduced to be responsible for the increased rate of copolymerization with AIBA. Both UPDS monomer and the copolymer of UPDS with diethyl fumarate were highly reactive towards 2-methoxyethylamine in aqueous medium, giving their corresponding amides in high yields.

(Keywords: polymerizable surfactant; active ester group; dialkyl fumarate)

INTRODUCTION

Many studies have been undertaken to elucidate the polymerization features of surface-active monomers above their critical micelle concentrations (*CMC*s)[1–11]. Much attention has also been devoted to surface-active monomers because of their applications as polymerizable emulsifiers[12–16]. Various types of polymerizable surfactants have been synthesized and used in emulsion polymerizations to obtain latex particles with chemically bonded emulsifiers at their surfaces. These monomers, bearing both a hydrophobic and a hydrophilic group, form molecular aggregates in aqueous media and apolar solvents. Monomer micellization has been found to accelerate polymerization for a number of systems, especially in aqueous micellar solutions[17]. Even low reactivity monomers bearing allyl groups such as sodium 10-undecenoate[18–21], 10-undecen-1-yl sulfate[22] and allyldimethyldodecylammonium bromide[23], have been demonstrated to form the corresponding polymers at concentrations above their *CMC*s, although their molecular weights are rather low. On the other hand, allyl monomers have been known to undergo alternating copolymerizations with electron-accepting monomers such as maleic anhydride and dialkyl fumarates. Therefore, it can be expected that alternating copolymers with high molecular weights will be produced by copolymerizations in micellar systems. However, little has been investigated about the effect of monomer micellization on copolymerizations, especially for alternating copolymerizations[24,25].

We have recently synthesized a polymerizable surfactant bearing an active ester group and an allyl group, *p*-10-undecenoyloxyphenyldimethylsulfonium methylsulfate (UPDS), and studied its aggregational behaviour in water and benzene solutions and its adsorption at water–air interfaces[26]. The hydrophilicity of the dimethylsulfonium methylsulfate group was found to be comparable to that of trimethylammonium bromide.

The present paper deals with the homopolymerization of UPDS and the copolymerization of UPDS with dialkyl fumarates (DRFs) in micellar, reverse micellar and isotropic solutions. The effects of the structure of the micellar aggregates and the kind of initiator on the kinetics and mechanism of the copolymerization and the characteristics of the resulting copolymers are investigated. The reactivity of the active ester groups in UPDS and the copolymers towards a primary amine in an aqueous medium is also examined.

EXPERIMENTAL

Materials

UPDS was synthesized through the condensation reaction of 10-undecenoic acid with *p*-hydroxyphenyldimethylsulfonium methylsulfate in the presence of dicyclohexylcarbodiimide in acetonitrile, and purified

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*To whom correspondence should be addressed according to the method described previously[26]. UPDS forms aqueous micelles in water and reverse micelles in benzene, and the *CMC*s are 3.0–6.5×10^{-3} and 3.6×10^{-2} M, respectively, at 25°C[26].

Diethyl fumarate (DEF), dibutyl fumarate (DBF) and dioctyl fumarate (DOF) were purchased from Tokyo Kasei and purified by distillation under reduced pressure. 2,2′-Azobis(2-amidinopropane) dihydrochloride (AIBA), a water-soluble radical initiator from Wako (reagent grade), was employed as received. 2,2′-Azobisisobutyronitrile (AIBN) from Wako was purified by recrystallization from methanol. 2-Methoxyethylamine (MOEA) was received from Tokyo Kasei and distilled before use.

Acetonitrile, ethyl acetate, dioxane and benzene were distilled after dehydration. Diethyl ether was used as received. Deionized water of a specific conductivity of $1\times10^{-6}\,\mathrm{S\,cm^{-1}}$ or lower was doubly distilled under a nitrogen atmosphere before use.

Homopolymerization

Homopolymerization of UPDS was carried out in aqueous micellar solutions at a concentration much higher than the *CMC*. The micellar solution of UPDS containing a radical initiator was kept at 60°C under a nitrogen atmosphere for one day. AIBA and AIBN were used as initiators. Water was removed from the reaction mixture by freeze drying. The solid was dissolved in a small volume of acetonitrile and the solution was poured into a large volume of ethyl acetate to dissolve unreacted UPDS monomer. Polymerized UPDS was collected by filtration and dried in a vacuum.

Copolymerization

Aqueous micellar copolymerization was conducted at 60°C in a sealed glass tube under a nitrogen atmosphere in the presence of a radical initiator. The reaction mixture was then freeze dried. Then, a small volume of acetonitrile was added to the residue and the solution was poured into a large volume of ethyl acetate. The precipitated copolymer was collected by filtration, washed several times with ethyl acetate and then diethyl ether, and dried in a vacuum. The level of conversion was gravimetrically determined.

The copolymerizations in benzene and dioxane solutions and in bulk were also carried out at 60°C in sealed glass tubes under a nitrogen atmosphere in the presence of a radical initiator. After an appropriate period of time, the contents of each tube were poured into a large volume of ethyl acetate containing a small amount of *p*-methoxyphenol. The resulting copolymers were isolated in the same manner as for aqueous micellar copolymerization.

Each copolymer composition was determined from the ratio of peak areas for the phenyl and ester groups in the ^{1}H n.m.r. spectrum and by elemental analysis. The glass transition and degradation temperatures of the copolymers were determined by differential scanning calorimetry (d.s.c.) and thermal gravimetry (t.g.), respectively, under a nitrogen atmosphere.

Molecular weight and molecular weight distribution

As gel permeation chromatography (g.p.c.) data for the cationic copolymers prepared in the present study could not be obtained owing to their adsorption onto polystyrene gels, neutral copolymers of methyl 10-undecenoate obtained by hydrolysis and subsequent methylation of the cationic copolymers were subjected to g.p.c. measurements. Each copolymer was first hydrolysed in dilute NaOH solution at room temperature. The alkaline solution was acidified with concentrated hydrochloric acid, and the precipitated polymer was filtered off and washed several times with water until the pH of the filtrate was neutral. The copolymer in the acid form was dissolved in benzene and methylated with a large excess of diazomethane in ether. The solution was stirred overnight at ambient temperature and then poured into a large volume of methanol. The precipitated polymer was filtered off and dried in a vacuum. The quantitative conversion to the methyl ester derivative was confirmed from i.r. and ^{1}H n.m.r. spectra.

*Reaction of UPDS and poly(UPDS-*co*-DEF) with amine*

The reactivity of the active ester groups of UPDS and poly(UPDS-*co*-DEF) was investigated by reaction with MOEA in water at 25°C. UPDS was dissolved in water to prepare a solution at a concentration of 0.1 M above the *CMC*. Then MOEA was added to the solution, and the mixture was stirred for 24 h. The reaction product of amidation was obtained as a white precipitate. The precipitate was filtered off, washed well with water and dried in a vacuum. The structure of the product was determined by i.r. and ^{1}H n.m.r. spectroscopy and elemental analysis. An aqueous solution of barium hydroxide was added to the filtrate to isolate the 10-undecenoic acid formed by hydrolysis as the barium salt, thus allowing the extent of hydrolysis to be determined.

The reaction of poly(UPDS-*co*-DEF) with the amine was conducted at a concentration of 0.1 M per UPDS unit under the same conditions as above. The product in the form of a precipitate was filtered off, repeatedly washed with water and dried in a vacuum.

Measurements

I.r. spectra were recorded on a JASCO IR-S1 spectrometer using KBr pellets. ^{1}H n.m.r. spectra were obtained on a JEOL JNM-EX270 spectrometer. Elemental analyses were performed using a Yanaco CHN MT-3 analyser. D.s.c. and t.g. measurements were performed on a SEIKO I SSC5000 thermal analyser. G.p.c. measurements were made using dimethylformamide as the solvent on a Toyo Soda HLC-802A chromatograph, and molecular weights were estimated based on calibration with standard polystyrene samples as references.

RESULTS AND DISCUSSION

Homopolymerization of UPDS

The homopolymerization of UPDS was unsuccessful with AIBN as initiator in some organic solvents, such as benzene, dioxane and dimethylformamide. The homopolymer was also not produced in micellar polymerization with AIBN in water. However, UPDS was found to homopolymerize in aqueous micellar solution using AIBA as initiator, giving the polymer in 5.6% yield. The mean molecular weight ($\overline{M}_w$) was 6100, corresponding to a degree of polymerization ($\overline{DP}$) of about 14. G.p.c. of the homopolymer showed that the polydispersity ($\overline{M}_w/\overline{M}_n$) was 1.18. The $\overline{DP}$ value is very close to

Table 1 Copolymerization parameters of UPDS (M_1) and two DRFs (M_2) at 60°C

M_2	Solvent	Initiator	r_1	r_2	r_1r_2	Q_1	e_1
DEF	Water	AIBA	0.014	0.041	5.74×10^{-4}		
	Water	AIBN	0.005	0.012	0.60×10^{-4}		
	Benzene	AIBN	0.015	0.042	6.30×10^{-4}	0.013^a	-0.45^a
DBF	Water	AIBA	0.046	0.068	31.30×10^{-4}		
	Water	AIBN	0.010	0.033	3.30×10^{-4}		
	Benzene	AIBN	0.013	0.100	13.00×10^{-4}		

[a] Q and e values of 0.25 and 2.26, respectively, for DEF were used for the calculation[29]

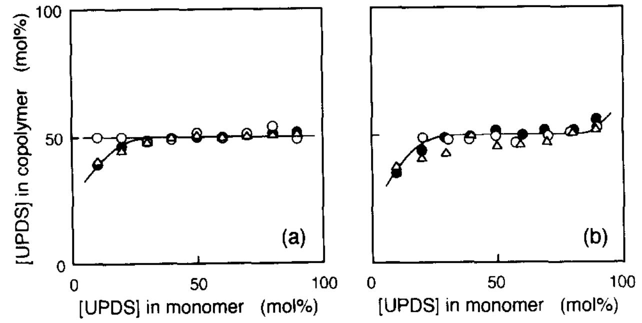


Figure 1 Results for copolymerizations of UPDS with (a) DEF and (b) DBF in water and benzene at 60°C ([UPDS] + [DRF] = 1.0 mol l^{-1}; [initiator] = 20 mmol l^{-1}): (●) water, AIBA; (○) water, AIBN; (△) benzene, AIBN

that of poly(sodium 10-undecenoate) formed by micellar polymerization under u.v. irradiation[20]. It has been reported that the $\overline{DP}$ of poly(sodium 10-undecenoate) is equal to the micellar aggregation number of monomeric micelles (N_S)[10,20,27]. On the other hand, the $\overline{DP}$ of poly(UPDS) is one third of the mean aggregation number of the monomeric micelles ($N_S = 42$)[26]. This may be ascribed to the density of molecules within the micelles. In our previous paper, it was demonstrated that N_S for UPDS micelles is considerably lower than that for other cationic surfactants with a comparable hydrophilic–hydrophobic balance[26]. This suggests a loose array of molecules in the micelles. Monomers with allyl groups as the polymerizable groups are well known to be susceptible to degradative chain transfer. The lower density of molecules within the micelles means that the acceleration effect on polymerization caused by molecular orientation will be absent. Thus, chain transfer becomes more significant, resulting in the formation of polymers with a degree of polymerization lower than the micellar aggregation number. The effect of initiators on the micellar polymerization of UPDS will be discussed later.

Copolymerizations of UPDS with DRFs

Copolymerizability of UPDS with DRFs. *Figures 1a* and *1b* show composition curves for the copolymerizations of UPDS with DRFs in water and benzene. The copolymerizations are characterized by a relatively high tendency towards alternation for both comonomer systems over a wide range of feed compositions. Both water-soluble AIBA and oil-soluble AIBN were used for the copolymerizations in water. The latter initiator was solubilized into aqueous micelles to initiate the copolymerization within the micelles. DEF was also solubilized into the micellar solution of UPDS under these conditions, and the monomer solution was apparently homogeneous over the whole range of feed compositions studied here. On the other hand, DBF was solubilized at a concentration of UPDS higher than 30 mol%, although the monomer solution was only faintly opaque at feed compositions of UPDS just below 30 mol%. Consequently, the copolymerizations in water proceeded exclusively within UPDS micelles. The copolymerization system in benzene was also homogeneous over the whole range of monomer compositions examined. The monomer reactivity ratios of UPDS (M_1) and the DRFs (M_2) were estimated by the Kelen–Tüdös method[28]. As summarized in *Table 1*, the values of r_1 and r_2 range from 0.005 to 0.046 and from 0.012 to 0.100, respectively, indicating that highly alternating copolymers are formed for the copolymerizations of UPDS with DRFs. The r_1r_2 values indicate that the micellar copolymerizations of UPDS with DRFs using AIBN as initiator yield more alternating copolymers compared with the respective copolymerizations with AIBA. The difference is pronounced at the higher feed compositions of the DRFs. The terminal double bonds of the UPDS molecules are located at the core of the micelle. The solubilized sites of the DRF will be distributed from the core to the palisade layers as the feed composition of the DRF is increased. Thus, the monomer composition at the core can be kept constant even at the higher feed compositions of the DRFs. The radicals from hydrophilic AIBA will initiate the copolymerization at the palisade layers and those from hydrophobic AIBN at the core. These are probably responsible for the highly alternating compositions of the copolymers produced at the higher feed compositions of the DRFs for the copolymerizations with AIBN.

As already mentioned, UPDS forms reverse micelles in benzene. Their aggregation number should be low in the absence of water. Therefore, an attempt to calculate Q and e values was made using the monomer reactivity ratios for the copolymerization with DEF in benzene. The Q value of UPDS is comparable to that of a typical non-conjugative monomer such as vinyl acetate. The e value is negative, indicating that UPDS is a donor monomer. As shown in *Figure 2*, the initial rate of copolymerization for UPDS with a DRF reveals a maximum at an equimolar composition of comonomers in the feed. This is typical for alternating copolymerizations between electron-donating and electron-accepting monomers.

Kinetic features of copolymerization: effect of solvents. Time–conversion curves for the copolymerization of UPDS with DEF in water, benzene, dioxane and in bulk at an equimolar comonomer composition in the

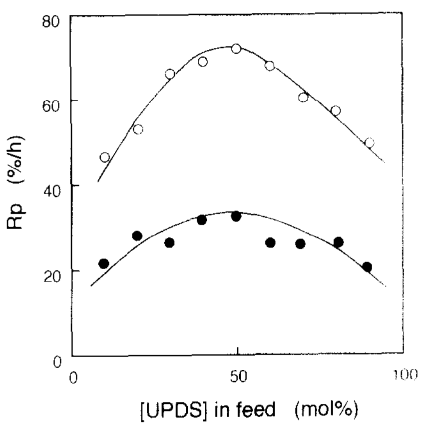


Figure 2 Rates of copolymerization of UPDS with DRFs in water at 60°C ([UPDS]+[DRF]=1.0 mol l^{-1}; [AIBA]=20 mmol l^{-1}): (○) DEF; (●) DBF

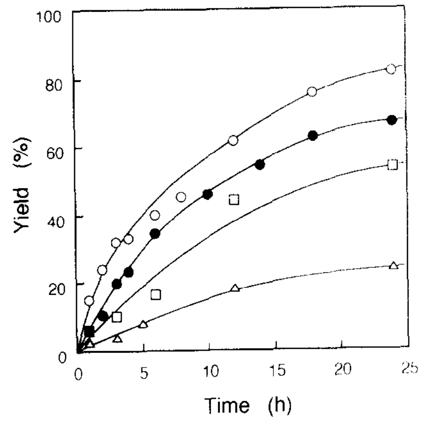


Figure 3 Results for copolymerizations of UPDS with DEF at 60°C ([UPDS]=[DEF]=0.5 mol l^{-1}; 2 mol% AIBN): (○) water; (□) benzene; (△) dioxane; (●) bulk

feed are shown in *Figure 3*. UPDS forms aqueous micelles and reverse micelles in water and benzene, respectively, above the *CMC*, as described in our previous paper[26], while the solution of UPDS in dioxane is isotropic. Since the concentration of UPDS in water is sufficiently higher than the *CMC*, DEF is completely solubilized into the micellar solution to form an apparently homogeneous solution. The rate of copolymerization in aqueous micellar solution is faster than that in the bulk, although the monomer concentrations within the micelles are comparable to those in the bulk. For the reverse micellar solution in benzene, the copolymerization rate is slower than that in the bulk, and faster than that in isotropic dioxane solution. Thus, the copolymerization in the micellar solution appears to be accelerated not merely by the locally high concentration of the monomers but also by the molecular orientation within the micelles.

Kinetic features of copolymerization: effect of comonomers. The time–conversion curves for the copolymerizations of UPDS with three kinds of DRF in various solvents are shown in *Figure 4*. DEF and DBF are solubilized into aqueous micellar solutions of UPDS under the conditions employed. The copolymerization of UPDS and DEF proceeds homogeneously over the whole range of conversions because the resulting copolymers are soluble in water. On the other hand, the copolymer of UPDS with DBF is not soluble in water, and hence the copolymerization yields a gelatinous solid that swells in water. The monomer solution of DOF in water is turbid in the initial stages of the copolymerization because DOF is not completely solubilized into the UPDS micelles. The copolymer is also gelatinous in water.

The rate of copolymerization in water increases with decreasing alkyl chain length of the DRF, as shown in *Figure 4a*. The time–yield curve for the copolymerization

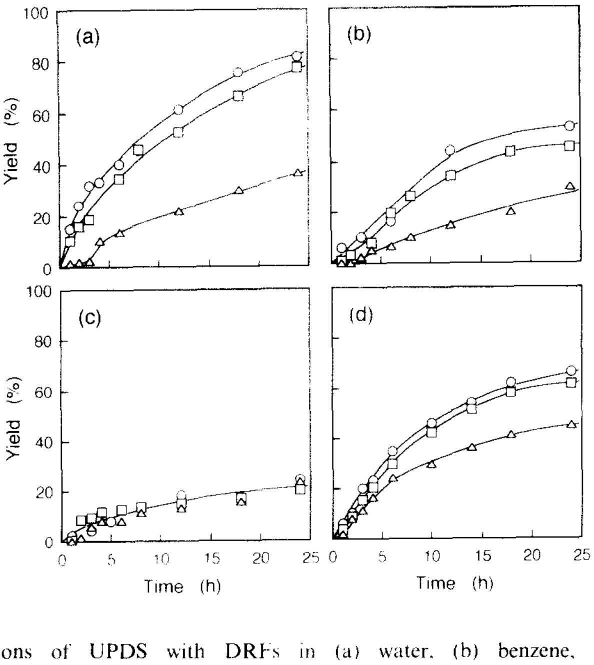


Figure 4 Results for copolymerizations of UPDS with DRFs in (a) water, (b) benzene, (c) dioxane and (d) bulk at 60°C ([UPDS]=[DRF]=0.5 mol l^{-1}; 2 mol% AIBN): (○) DEF; (□) DBF; (△) DOF

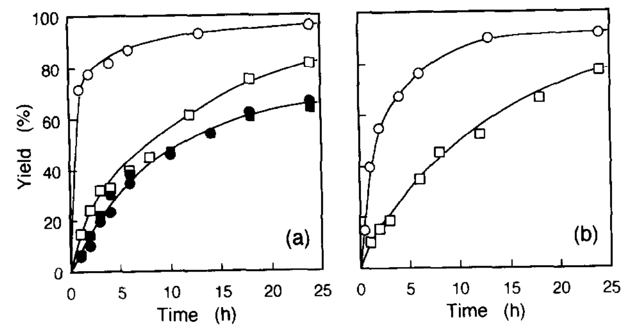
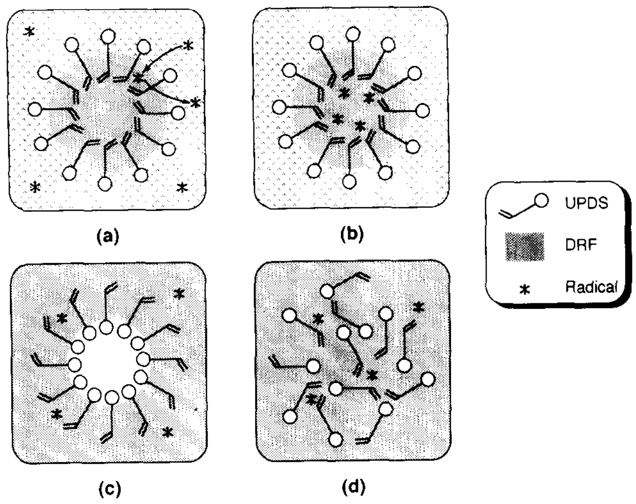


Figure 5 Results for copolymerizations of UPDS with (a) DEF and (b) DBF at 60°C: (○) water, AIBA; (□) water, AIBN; (●) bulk, AIBA; (■) bulk, AIBN

with DOF is S-shaped, which is typical for an emulsion polymerization. This would result from the fact that DOF, which is not solubilized in the initial stages of polymerization, is incorporated into the micelles during the copolymerization.

The monomer solutions in benzene and dioxane were homogeneous and the copolymerizations also proceeded homogeneously over the whole range of conversions. The rate of copolymerization in benzene also increases with decreasing alkyl chain length of the DRF, as shown in *Figure 4b*. The tendency is very similar to that for the copolymerization in the bulk, shown in *Figure 4d*. On the other hand, *Figure 4c* shows that the rate is little dependent on the type of DRF for the copolymerizations in dioxane. It has been demonstrated that the homopolymerizability of DRFs with linear alkyl ester groups in the bulk changes little or slightly decreases with increasing length of the ester alkyl group[30,31]. The rate of alternating copolymerization has been recognized to increase with an increase in the interaction between the propagating radical and the monomer in the cross-propagation. Such interaction should be related to the distance between interacting species, which is variable with the monomer concentration and the polarity of the medium. The intermolecular distance should be short in aqueous micellar and reverse micellar solutions and in the bulk compared with that in isotropic dioxane solution, and hence the steric influence of the alkyl group in fumarates will become more pronounced.



Scheme 1 Schematic representation of the copolymerizations of UPDS with DRF: (a) water, AIBA; (b) water, AIBN; (c) benzene, AIBN; (d) dioxane or bulk, AIBN

Kinetic features of copolymerization: effect of initiators. The time–yield curves for the copolymerizations of UPDS with DRFs in water using two kinds of initiators (AIBA and AIBN) are presented in *Figure 5*. The copolymerizations with AIBA are definitely faster than those with AIBN for both comonomers used here. Since there is little difference between the rates of copolymerization in the bulk with AIBA and AIBN, the differences in the rates of copolymerization in water could be related to differences in the rates of termination. AIBN decomposes inside micelles to generate primary radicals. It can be presumed that the radicals little diffuse from the micelles because of their hydrophobicity. On the other hand, primary radicals from the hydrophilic initiator AIBA get into the micelles from the water phase to initi-

Table 2 Data for radical copolymerizations of UPDS with DRFs in various solvents[a]

DRF	Solvent	Initiator	Yield (%)	$\overline{DP}^b$	$\overline{M}_w/\overline{M}_n{}^b$
DEF	Water	AIBA	96	185	1.4
		AIBN	82	93	1.4
	Benzene	AIBN	54	86	1.4
	Dioxane	AIBN	24	73	2.3
	Bulk	AIBN	64	83	2.1
DBF	Water	AIBA	92	224	1.4
		AIBN	78	121	1.3
	Benzene	AIBN	46	115	1.7
	Dioxane	AIBN	20	121	2.7
	Bulk	AIBN	58	130	2.7
DOF	Water	AIBA	58	57	2.2
		AIBN	37	52	2.4
	Benzene	AIBN	30	47	1.9
	Dioxane	AIBN	23	52	2.5
	Bulk	AIBN	44	54	2.5

[a] [UPDS] = [DRF] = 0.5 mol l^{-1}, 2 mol% initiator with respect to monomers; 60°C; 24 h
[b] Determined by g.p.c.

Table 3 Thermal properties of poly(UPDS-*co*-DRF)s[a] and the corresponding homopolymers

		Degradation temperature (°C)		
DRF	T_g(°C)	Initial	Maximum	Reference
None	−60	200	245	This work
DEF	−5	200	348	This work
DBF	−17	202	348	This work
DOF	−31	199	346	This work
Homopolymers				
DEF	40	243	382	32
DBF	8	260	378	32
DOF	−6	244	384	32

[a] Alternating copolymers of UPDS with DRFs

ate the copolymerization inside the micelles. Only one radical can stay in one micelle, and the copolymerization continues to propagate until another radical enters the micelle. Cationic charges on the micelle prevent a cationic primary radical from going into the micelle. Thus, the rate of termination is depressed, resulting in an increased rate of copolymerization, as illustrated in *Scheme 1*. A similar mechanism might be suggested for the homopolymerization of UPDS.

Molecular weights of copolymers

Table 2 gives the yields and molecular weights of the copolymers obtained by the copolymerizations of UPDS with DRFs at equimolar compositions in the feed under various conditions. The molecular weight distributions of copolymers formed in aqueous micellar solution are relatively narrow. On the other hand, the values of $\bar{M}_w/\bar{M}_n$ for the copolymers with DOF are high, probably because DOF is not completely solubilized into the micelles of UPDS. In addition, the values of $\bar{M}_w/\bar{M}_n$ for copolymers produced in reverse micellar solutions are lower than those for copolymers yielded in isotropic solution and in the bulk. Thus, the formation of micelles and reverse micelles affects the molecular weight distributions of the resulting copolymers, as has also been shown for homopolymerization.

The copolymerizations with DEF and DBF in aqueous micellar solutions using AIBA as initiator also give copolymers having high molecular weights in comparison with those obtained in other systems. On the other hand, the values of $\overline{DP}$ for the copolymers formed in benzene, dioxane and water using AIBN as initiator are close to those for the copolymers produced in the bulk. Therefore, the molecular weight of the copolymer is not related to the overall concentration of monomers in the feed. Free radicals from AIBA outside the micelles could react with the propagating radicals with a lower frequency in contrast with those from AIBN, resulting in a higher degree of polymerization. This would also support the schematic model proposed above.

Thermal properties of polymers of UPDS

Table 3 shows the thermal properties of the homopolymer of UPDS and the alternating copolymers of UPDS with DRFs obtained by copolymerizations in aqueous micellar solutions using AIBA as initiator. The glass transition temperatures (T_g) decrease with increasing alkyl chain length of the DRF. The values of T_g for the copolymers are between those for the respective homopolymers of UPDS and the DRFs[32] contained therein.

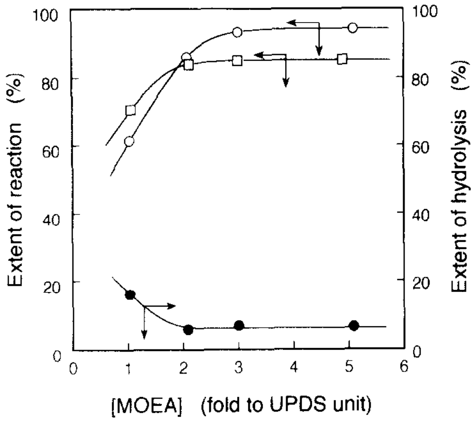


Figure 6 Results for reactions of UPDS and poly(UPDS-*co*-DEF) with 2-methoxyethylamine: (○, ●) UPDS; (□) poly (UPDS-*co*-DEF)

The initial degradation temperatures of the alternating copolymers are about 200°C, which is the same as the initial degradation temperature of the homopolymer of UPDS. Therefore, the initial degradation temperature seems to be related to the temperature at which UPDS units degrade. The maximum degradation temperatures of the copolymers are higher than the maximum degradation temperature of the homopolymer of UPDS and lower than those of the corresponding homopolymers of the DRFs[32].

*Reaction of UPDS and poly(UPDS-*co*-DEF) with amine*

UPDS has an active ester group in the molecule which can react with primary amines under mild conditions, as described in our previous paper[26]. Here, comparative studies of the reactivities of UPDS and its copolymer with DEF were performed using 2-methoxyethylamine (MOEA) as the water-soluble amine. Poly(UPDS-*co*-DEF) was used for the reaction with the amine because only this copolymer is soluble in water among the copolymers of UPDS with DRFs. As shown in *Figure 6*, the extent of reaction of UPDS increases with increasing concentration of MOEA in the feed. UPDS gave the amide derivative in 94% yield in the reaction at a molar ratio of MOEA to UPDS above 3. In the reaction, the amidation is accompanied to some extent by hydrolysis. About 6% of UPDS was hydrolysed at a molar ratio above 2. On the other hand, poly(UPDS-*co*-DEF) exhibits an extent of amidation of 85% at a molar ratio of MOEA to UPDS above 2, which is a slightly lower extent of amidation than that for UPDS monomer. The white sticky precipitate appeared immediately after MOEA was added to the copolymer solution since the amidated product is insoluble in water. The precipitate was found to contain unreacted UPDS units. No carboxylic acid or carboxylate peaks were observed in the i.r. spectrum of the amidated product. Therefore, little hydrolysis of the active ester group takes place in the reaction of the copolymer. This could be attributed to a rapid amidation followed by precipitation of the product, which makes unreacted UPDS units remain intact.

As described above, UPDS undergoes alternating copolymerizations with DRFs at a considerably high rate in the molecularly aggregated state in water. We attempted seeded copolymerizations of UPDS adsorbed onto the surfaces of polymeric microspheres with DRFs incorporated into the microspheres in order to obtain reactive microspheres bearing active ester groups on their surfaces. We are going to report the results in the near future.

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