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New AB or ABA type block copolymers: atom transfer radical polymerization (ATRP) of methyl methacrylate using iodine-terminated PVDFs as (macro)initiators

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Summary

PMMA homopolymer with $CF_3(CF_2)_2CF_2$- end group was prepared by the ATRP of MMA using $CF_3(CF_2)_2CF_2$-I as an initiator and coppe (I) salts/bipy catalysts. This indicated the production of perfluorobutyl radicals by ATRP mechanism and successful polymerization by them. Di- and triblock copolymers were also prepared by the ATRP of MMA using iodine-terminated PVDF as (macro)initiators. The kinetic plots ($In[M]_o/[M]$ *vs.* time) showed nearly first-order with respect to monomer concentration and the $M_{n,NMR}$ of block copolymers increased linearly with conversion. However, iodine-terminated PVDF showed low initiator efficiency because propagating rate was much faster than initiating rate

Introduction

Poly(vinylidene fluoride)(PVDF) has outstanding resistance to weathering and chemical, melt process, and wide practical use(coating materials, electrical/electronic component, chemical processing components such as piping, tank linings, filtration, etc.). However, it practically has no adhesion properties to other materials. Hence, physical modifications by blending PVDF with various polymers have been investigated, but application range is extremely restricted because there are few polymers having adhesion properties or compatibility with PVDF. Although poly(methyl methacrylate)(PMMA) has good compatibility with PVDF, blend of them lacks flexibility and has poor adhesion to metals because the glass transition temperature of PMMA is very high as compared with that of PVDF(1).

Controlled/ 'living' radical polymerizations appeared to be a powerful tool of controlling molecular weights, polydispersities, end groups, and chain architectural composition, etc.. The synthesis of block copolymers usually requires efficient controlled/ 'living' polymerization(2). In recent years stable nitroxyl radical systems and atom transfer radical polymerization(ATRP) have given new and efficient ways to conduct controlled/ 'living' radical polymerizations of nonfluoro vinyl monomers such as styrene, methacrylate, and their derivatives(3-7). ATRP with a variety of alkylbromide (or chloride), as initiator and transition metal complex of suitable ligands, as catalyst, seems to be the most versatile in terms of diversity of monomers.

'Iodine' transfer polymerization(ITP) is commercially very important for production of well-defined fluoropolymers in a 'living' fashion(8-10). However, it have been

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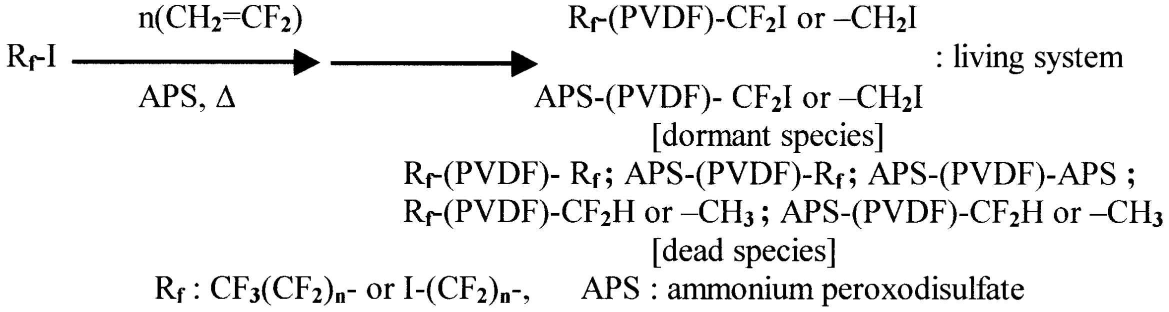
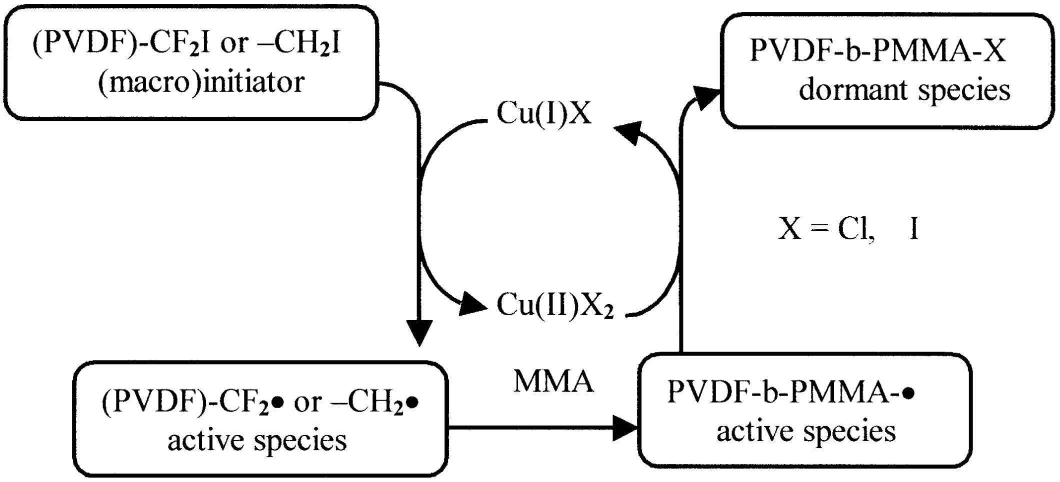
unsuccessful to obtain the block copolymers of fluoropolymers and nonfluoro polyacrylate by ITP because the reactivity of perfluorocarbon radical with respect to acrylate monomers is low(11).

Shenkang et al. recently prepared the ABA type block copolymer from ATRP of styrene using bromine-terminated PVDF oligomer as (macro)initiator(12), but the bromine-terminated PVDF with high molecular weight cannot be easily obtained. The iodine-terminated PVDF with high molecular weight and well-defined structure can easily be prepared by ITP because CF_2-I bond is weaker than CF_2-Br bond, but in the typical ATRP alkyl iodide or perfluoroalkyl iodide has not been used as an initiator. The preparation of AB or ABA type block copolymers of PVDF and PMMA from the ATRP using iodine-terminated PVDF as (macro)initiator is not reported yet.

To develop new material which is expected to have better adhesion than flurorpolymers, block copolymers are prepared by a combination of ITP (Scheme 1) with ATRP of MMA using iodine-terminated PVDFs as (macro)initiators (Scheme 2).



Scheme 1. Iodine Transfer Polymerization(ITP) for the iodine-terminated PVDF.



Scheme 2. Atom Transfer Raical Polymerization(ATRP) for block copolymerization.

Experimental

Materials: Ammonium peroxodisulfate(APS), 2,2'-bipyridine(bipy), *N*,*N*'-dimethyl-acetamide(DMAc), and methyl methacrylate(MMA) were purchased from Aldrich Chemical Co. Perfluorobutyl iodide(98%), 1H, 1H-heptafluorobutyl iodide(97%), and 1,4-diiodo-perfluorobutane(97%) were purchased from Fluoro Chemical Co. CuBr and CuCl were purified with glacial acetic acid and anhydrous ethanol. Vinylidene fluoride(VDF) was prepared by thermolysis of 1-chloro-1,1-difluoroethane in our laboratory and purified to high purity of above 99.98%.

Characterization: Monomer conversion was determined by GC(Varian VISTA 6000) with flame ionized-detector and 80/100 CHROMOSORB WAW stainless steel columns. NMR spectra were obtained from Varian 60OMHz NMR spectrometer. Thermal transition temperature was determined by DSC(Perkin-Elmer DSC7). GPC chromatograms of iodine-terminated PVDF and block copolymers were obtained by using Shodex GPC columns(KF-800, 801, 802, 802.5), Alltech 500 ELSD (evaporative light-scattering detector, Drift tube temp: 90 °C), and THF as eluent. Polystyrene standards were used to calibrate the columns. Iodine functionality of iodine-terminated PVDF was determined by X-ray Fluorescence Spectrometry(XRF) Model PW1480 using 2% indium as internal standard.

Synthesis of iodine-terminated PVDF by ITP: In 300mL Parr reactor, 150 g of deionized water were charged. After degassing of the reactor and charging with argon, 12 mmole of perfluorobutyl iodide (or 6 mmole of 1,4-diiodoperfluorobutane) and 0.6 mmole of APS were added. 350 psi of VDF was initially introduced. And then the reactor was heated to 80 °C. After beginning of the polymerization, subsequent addition of VDF was continued to maintain constant pressure throughout the polymerization. After about 20 hours, polymerization was stopped by venting unreacted monomer. Polymer was obtained by coagulating the latex, washing, and drying.

Table 1. Molecular weights of the iodine-terminated PDVF

Samples	M_n	M_p	M_w/M_n	Iodine functionality[b]	Method
PVDF-I	4889	7858	1.61(1.37[a])		GPC
	3225				NMR
	4879			0.99	XRF
I-PVDF-I	6705	10539	1.94(1.29[a])		GPC
	5248				NMR
	5176			1.99	XRF

a : obtained by GPC using DMAc/0.05M $LiNO_3$ as eluent

b : the average-number of the iodine terminal per iodine-terminated PVDF molecule

ATRP of MMA using perfluorobutyl iodide or 1H, 1H-heptafluorobutyl iodide as initiators: 0.934 mmole of perfluoroalkyl iodide, 0.934 mmole of CuX(X=Br, Cl, I) and 1.868 mmole of bipy were added to 250 mL schlenk flask. After removal of oxygen within the flask, 93.4 mmole of MMA and 15 mL DMAc were introduced. And then reaction flask was immersed in an oil bath of 90 °C. At time intervals, the same amount of samples were taken out from the flask and diluted with DMAc for determining monomer conversion. And also diluted samples were injected for GPC analysis after removal of metal complex by passing through active alumina column.

Block copolymerization : ATRP of MMA using iodine-terminated PVDFs as (macro) initiators; 0.934 mmole of PVDF-I, 0.934 mmole of CuCl, and 1.868 mmole of bipy (or 0.934 mmole of I-PVDF-I, 1.868 mmole of CuCl, and 3.736 mmole of bipy) were added to 250 mL schlenk flask. After removal of oxygen within the flask, 46.7 mmole of MMA and 15 mL DMAc were introduced. The reaction flask was then immersed in an oil bath of 90 °C. At time intervals, the same amount of samples were taken out from the flask and diluted with DMAc for determining monomer conversion. And also diluted samples were injected for GPC analysis after removal of metal complex by passing through active alumina column. Diluted samples were also poured into methanol and recovered polymers were used for NMR analysis.

Results and discussion

1. Synthesis of iodine-terminated PVDF by iodine transfer polymerization (ITP):

As shown in Fig. 1, $-CF_2CH_2I$ and $-CH_2CF_2I$ end groups of iodine-terminated PVDF (PVDF-I and I-PVDF-I) were observed at 3.8 ppm and 3.6 ppm, respectively. $-CH_2CF_2H$ and $-CF_2CH_3$ end groups as dead species were also observed. Main dormant species in iodine transfer polymerization of VDF is expected to be $-CH_2CF_2$-I, but small amount of $-CF_2CH_2I$ end group by head-to-head or tail-to-tail inversion is also expected(13). However, the intensity of $-CF_2CH_2$-I peak in Fig.1 was higher than that of $-CH_2CF_2$-I. peak because the bond dissociation energy of CF_2CH_2-I was higher than that of CH_2CF_2-I. Actually, $-CH_2CF_2$-I end group was almost changed to $-CF_2CH_2I$ end group after longer polymerization time. The M_n of iodine-terminated PVDF was estimated from the integration ratios of $[-CH_2CF_2\text{-}+\text{-}CF_2CH_2\text{-}]/[-CF_2CH_2I+\text{-}CH_2CF_2I]$ peaks in ^1H NMR spectra and the iodine functionality was determined by XRF. As listed at Table 1, the iodine functionality of I-PVDF-I was close to two times of PVDF-I.

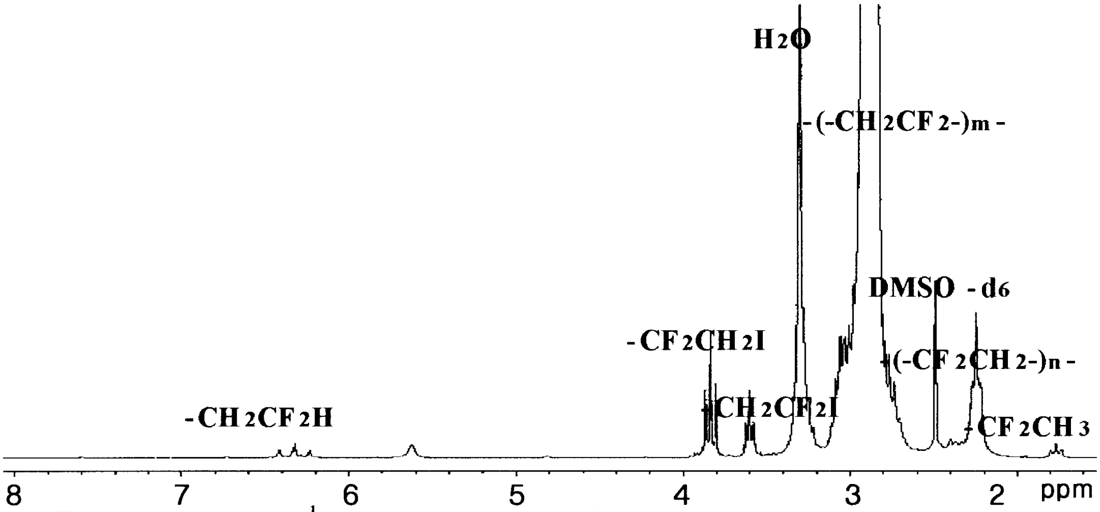


Fig. 1. 600MHz ^1H NMR spectrum of typical iodine-terminated PVDF.

2. ATRP of MMA using perfluoralkyl iodide as an initiator:

At first, ATRP of MMA using perfluoroalkyl iodide with $-CF_2CH_2I$ or $-CH_2CF_2I$ end groups, as initiators and various copper(I) salts/bipy catalysts was investigated because iodine-terminated PVDF had all of $-CF_2CH_2I$ and $-CH_2CF_2I$ end groups as shown in Fig.1. ATRP of MMA using $[CF_3(CF_2)_2CH_2I]$/[CuBr]/[bipy] catalytic system was slowly proceeded(conv.; 54% after 24hrs), but the kinetic plots of In$[M]_o/[M]$ *vs.* time showed the linearity. That is, $-CF_2CH_2I$ end group also acted as an initiator for ATRP.

In the case of $CF_3(CF_2)_2CF_2$-I initiator, polymerizations using either [CuBr]/[bipy] or [CuCl]/[bipy] catalysts were rapidly proceeded(conv.; 84% after 8hrs), but that using [CuI]/[bipy] catalyst was slowly proceeded(conv.; 55% after 24hrs). The first-order kinetic plots of all polymerizations using $CF_3(CF_2)_2CF_2$-I initiator showed curvature. Fig.2 showed the $M_{n,GPC}$ trend of the entire reaction mixture including polymeric product and $CF_3(CF_2)_2CF_2$-I initiator with the increase of MMA conversion. $M_{n,GPC}$ plots *vs.* conversion showed large deviation from the theoritical molecular weights ($M_{n,th}$= conv. x $FW_{monomer}$ X $[M]_o/[I]_o$ + $FW_{initiator}$). Although the $M_{n,GPC}$ in Fig.2 was the overall $M_{n,GPC}$ of the entire sample, this indicated the M_n of polymeric product because $CF_3(CF_2)_2CF_2$-I initiator peak was not included in polymer peak of GPC chromatograms. In the case of typical ATRP, the total number of the polymer chain almost remains constant because of fast initiation and slow propagation throughtout the polymerization, then the M_n is proportional to conversion. However, Fig.2 showed a very sharp decrease in the $M_{n,GPC}$

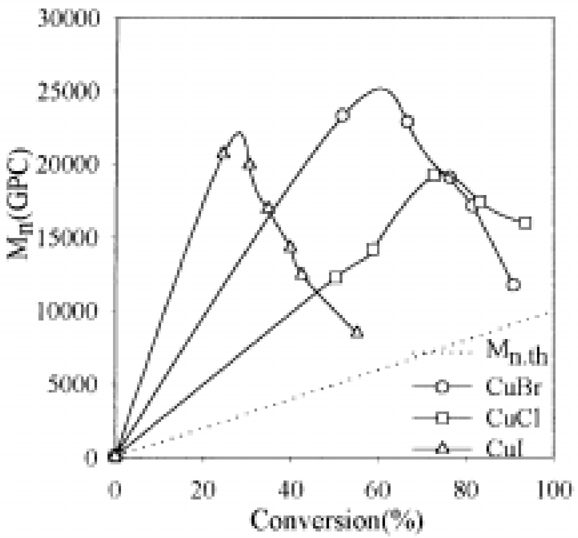


Fig. 2. Dependence of M_n(reaction mixture) on conversion for the ATRP of MMA using $CF_3(CF_2)_2CF_2$-I as an initiator in DMAc at 90°C. ($[MMA]_o/[Initiator]_o/[CuX]_o/[bipy]_o$ 100/1/1/2, X = Br, Cl, I)

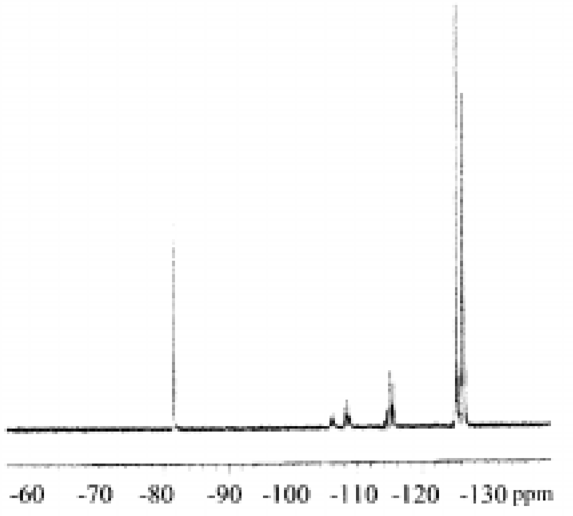


Fig. 3. ^{19}F-NMR spectrum of PMMA with $CF_3(CF_2)_2CF_2$- end group prepared by the ATRP of MMA using $CF_3(CF_2)_2CF_2$-I as an initiator in DMAc at 90°C. ($[MMA]_o/[Initiator]_o/[CuCl]_o/[bipy]_o$ = 100/1/1/2)

with MMA conversion, indicating increase of the total number of the polymer chain during the polymerization. This might result from slow initiation due to low initiating efficiency of [$CF_3(CF_2)_2CF_2$-I]/[CUX](X=Br, Cl, I)/[bipy] catalytic system with respect to MMA. Among them, [CuCl]/[bipy] catalyst showed better initiating efficiency when compared with other copper salts.

Fig.3 showed ^{19}F-NMR spectrum of the purified PMMA product which was obtained from the ATRP of MMA using $CF_3(CF_2)_2CF_2$-I initiator. $CF_3(CF_2)_2CF_2$- end group was observed at 81.6 ppm(CF_3-), 126.4 and 125.7 ppm(-CF_2-), and 114-115.6 ppm(-CF_2-CH_2-), but -CF_2-I (60 ppm) peak of $CF_3(CF_2)_2CF_2$-I initiator did not observed in Fig.3. These results meant the production of perfluorobutyl radicals by ATRP mechanism and successful polymerization of MMA by them. Therefore, successful ATRP of MMA using iodine-terminated PVDFs as (macro)initiators is expected, which means the production of block copolymers.

3. ATRP of MMA using iodine-terminated PVDsF as (macro)initiators

ATRP of MMA using iodine-terminated PVDF (macro)initiators and [CuCl]/[bipy] catalyst was carried out under the initial condition of $[MMA]_o/[(macro)initiator]_o/[CuCl]_o/[bipy]_o$=50/1/1/2(Scheme 2). As shown in Fig.4(A), the plots of $In[M]_o/[M]$ *vs.* time indicated that polymerizations were nearly first-order with respect to monomer concentration and the concentration of active species remained almost constant at below 80% of MMA conversion. However, some deviation from first-order kinetic plots at above 80% of MMA conversion was observed because of loss of 'living' nature by transfer or termination. ATRP using I-PVDF-I (macro)initiator was much faster than that using PVDF-I at the same ratio of $[MMA]_o/[(macro)initiator]_o$ because the iodine functionality of I-PVDF-I was almost two times higher than that of PVDF-I. Fig. 4(B) showed the overall $M_{n,NMR}$ trend of the entire reaction mixture including reaction product and unreacted (macro)initiator with the increase of MMA conversion. The overall $M_{n,NMR}$ increased linearly with conversion because the total number of the polymer chain including unreacted (macro)initiator should be remained constant if there was no

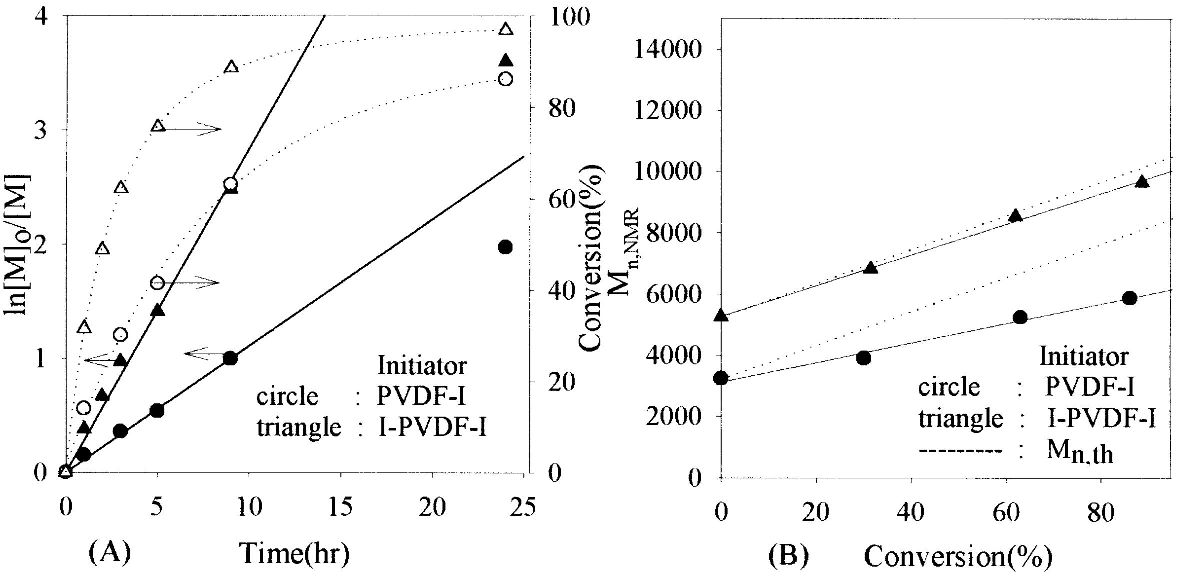


Fig. 4. Kinetic plots(A) and $M_{n,NMR}$ plots *vs*. conversion(B) for the ATRP of MMA using I-PVDF[$M_{n,NMR}$ 3225($M_{p,GPC}$ 7858)] and I-PVDF-I[$M_{n,NMR}$ 5248($M_{p,GPC}$ 10532)] as (macro)initiators in DMAc at 90°C. $[MMA]_o/[(macro)initiator]_o/[CuCl]_o/[bipy]_o$=50/1/1/2.

termination or chain transfer. The $M_{n,NMR}$ in the case of I-PVDF-I (macro)initiator was closed to the theoretical values, while that in the case of PVDF-I (macro)initiator was lower than the predicted values at higher conversion. Generally, the controlled/ 'living' radical polymerization is not true 'living' polymerization, and so some deviation from theoretical values because of transfer or termination is observed at high ratio of $[M]_o/[I]_o$. Hence, ATRP using PVDF-I at the same ratio of $[MMA]_o/[(macro)initiator]_o$ was thought to proceed more slowly and shown the lower molecular weights than theoretical values, when compared with I-PVDF-I.

Fig. 5 showed GPC traces of reaction mixtures obtained from the ATRP of MMA using PVDF-I [$M_{n,NMR}$ 3225($M_{p,GPC}$ 7858)] and I-PVDF-I [$M_{n,NMR}$ 5248($M_{p,GPC}$ 10532) as (macro)initiators and showed bimodal patterns. The intensities of PVDF-I and I-PVDF-I peaks rapidly decreased with increase of polymerization time, while new peaks at $M_{p,GPC}$=57300 and $M_{p,GPC}$=96258 appeared. These new peaks might be PVDF-PMMA and PMMA-PVDF-PMMA block copolymers. Further decrease of (macro)initiator peak did not observed after 10 hrs(PVDF-I: 70% of MMA conversion, I-PVDF-I: 90% of MMA conversion). These residual initiator peaks are thought to be unreacted (macro)initiator or PVDF homopolymer with -CF_2H end group, dead species, etc.. Polymerization of MMA under the same condition, which was $[MMA]_o/[CuCl]_o/[bipy]_o$= 100/1/2 in DMAc at 90 °C without (macro)initiator, was very slowly proceeded(conv.; 27.8% after 16hrs) and resulted in the production of PMMA homopolymer with $M_{n,GPC}$ =200,000. If the (macro)initiator radical, which is produced by ATRP mechanism, can not initiate the polymerization of MMA, the coupling products of (macro)initiator radical or PMMA homopolymer by the reverse ATRP mechanism(14) may be produced. However, any additional peaks, which correspond to PMMA homopolymer with $M_{n,GPC}$= 200,000 or PVDF homopolymer by coupling reactions, were not observed in GPC traces of Fig. 5. The bimodal peaks in GPC trace of Fig.5 might result from low initiator efficiency due to much faster propagating rate than initiating rate. Actually, the reactivity of perfluorocarbon radical with respect to monomers such as (meth)acrylate, acrylonitrile, etc., has known to be very low(11). The new peaks in GPC trace of Fig.5 could not completely separate from (macro)initiator peaks, but they showed very low

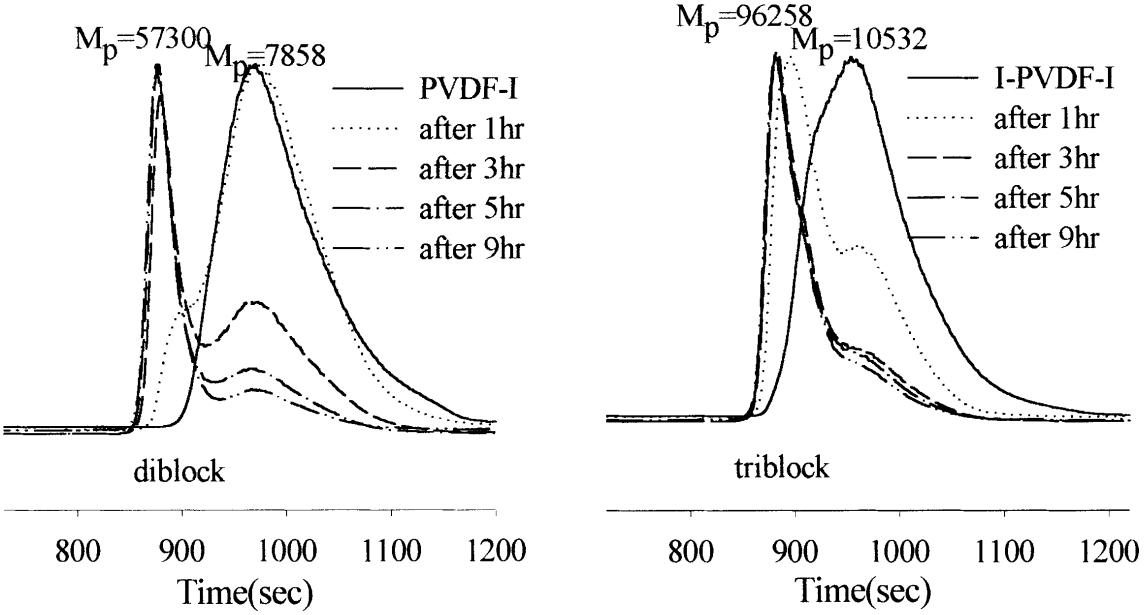


Fig. 5. GPC traces of reaction mixtures obtained from the ATRP of MMA using PVDF-I[$M_{n,NMR}$ 3225($M_{p,GPC}$ 7858)] and I-PVDF-I[$M_{n,NMR}$ 5248($M_{p,GPC}$ 10532) as (macro)initiators in DMAc at 90°C. $[MMA]_o/[(macro)initiator]_o/[CuCl]_o/[bipy]_o=50/1/1/2$.

polydispersities when compared to those of (macro) initiators.

As shown in Fig.6, ^{1}H NMR spectrum of reaction mixture in Fig.5(I-PVDF-I: 90% of MMA conversion after 9 hrs) showed the presence of PVDF segment with high intensity, while intensity of (macro)initiator peak in GPC chromatograms was very low. MMA/VDF mole ratios of these reaction mixture were calculated from intergration ratio of CH_2CF_2-[(e) and (e')] of PVDF segment and -OCH_3[(c-d)] of PMMA segment in ^{1}H NMR spectra. And also the $M_{n,NMR}$ in Fig. 4(B) were determined from these ratios. The MMA/VDF mole ratios of reaction mixtures in polymerization using PVDF-I and I-PVDF-I (macro)initiators in Fig.5 were 0.46 and 0.60 after 9hrs, respectively. As shown in Fig.3, PMMA with $CF_3(CF_2)_3$- end group was also prepared by the ATRP of MMA using $CF_3(CF_2)_3$-I as an initiator. Therefore, the new polymeric products obtained from the ATRP of MMA using PVDF-I and I-PVDF-I as (macro)initiators are thought to be PVDF-PMMA and PMMA-PVDF-PMMA block copolymers, respectively, although GPC chromatograms of these polymers showed bimodal peaks and some deviation from ideal ATRP because of low initiator efficiency of iodine-terminated PVDF was observed.

DSC pattern of triblock copolymer were almost similar to those of diblock copolymer. Fig.7 showed DSC thermograms of triblock copolymers. The glass transition temperature of amorphous PMMA homopolymer was observed at about 124°C. Generally, the glass transition temperature (T_g) and the melting temperature (T_m.) of PVDF homopolymer have known to be about - 40°C(measured by dilatometry) and 154-184°C, respectively(1). T_m of I-PVDF-I was found at 174°C and T_g was not observed. Though T_g of triblock copolymer was not clear, it seemed to be increased with increase of the molecular weights of PMMA segment. The melting peak of triblock copolymer seemed to decrease with increase of the molecular weights of PMMA segment. Actually, the melting peak of triblock copolymer with PMMA segment of M_n=4393 was completely disappeared.

Conclusions

The ATRP of MMA using $CF_3(CF_2)_2CF_2$-I initiator and copper(I) salt/bipy catalysts showed a very sharp decrease in $M_{n,GPC}$ with MMA conversion, indicating increase of

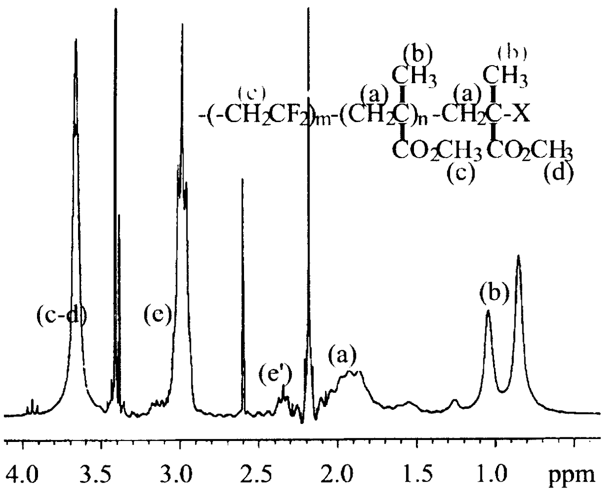


Fig. 6. ^{1}H NMR spectrum of block copolymer prepared by ATRP of MMA using I-PVDF-I [$M_{n,NMR}$ 5248 ($M_{p,GPC}$ 10532)] as (macro)-initiator. (90% of MMA conv. after 9 hrs)

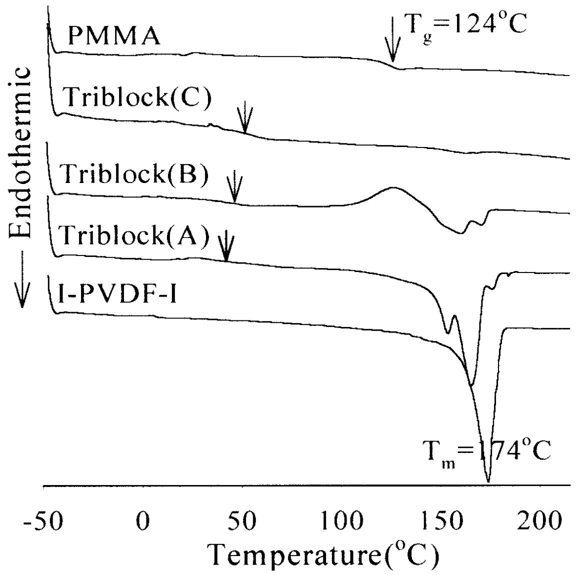


Fig. 7. DSC curves of PMMA, I-PVDF-I ($M_{n,NMR}$ 5248), and triblock copolymers ($M_{n,NMR}$ of PMMA segment in triblock : (A) 1561, (B) 3264, and (C) 4393)

the total number of the polymer chain during the polymerization because of slow initiation due to low initiator efficiency. But the $CF_3(CF_2)_2CF_2$- end group was observed at the PMMA homopolymer. These results meant the production of perfluorobutyl radicals by ATRP mechanism and successful polymerization of MMA by them.

PVDF-PMMA and PMMA-PVDF-PMMA di- or triblock copolymers were also prepared by the ATRP of MMA using iodine-terminated PVDF (PVDF-I and I-PVDF-I) as (macro) initiators. : The nearly first-order kinetic plot and linear increase of the $M_{n,NMR}$ plot *vs.* conversion were observed, but GPC traces showed bimodal peaks due to low initiator efficiency of (macro)initiator. However, PVDF segment with high intensity in ^{1}H-NMR spectrum of block copolymer was observed.

The glass transition temperature of triblock copolymer seemed to increase with increase of the molecular weights of PMMA segment. However, the melting peak of triblock copolymer decreased with increase of the molecular weights of PMMA segment.

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