Review

Stimulation on the addition reactivity of fluorinated vinyl monomers—Facile carbon–carbon bond formation by the aid of fluorine substituents

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ABSTRACT

The high addition reactivity of fluorinated vinyl compounds toward radical and anionic species was demonstrated to afford facile methods for the carbon–carbon bond formation by the aid of fluorinated substituents of vinyl groups. Some of the reactions are proved to be applicable to the preparation of polymers by radical or anionic polyaddition reaction mechanism. The investigation on the anionic reactivity order of fluorinated acrylates and methacrylates may contribute to the development in the field of the estimation by the computer chemistry to determine which effect of the fluorine-substitution would control the reactions.

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1. Introduction

One of the most important organic reactions would be carbon–carbon bond formation reactions. It is the key strategy in organic syntheses to build a framework of a compound to be desired. Quite a few reactions which yield carbon–carbon bonds have been reported since 19th century and the exploration on the carbon–carbon bond formation should be still continued because the information on the reactions is not enough to satisfy synthetic organic chemists. The propagation reaction in the addition polymerization of vinyl monomers is one of the carbon–carbon bond formation reactions. Polymers are yielded by the repetition of carbon–carbon bond formation reactions at living ends with vinyl monomers several times.

The investigation on anionic polymerization reactivity of fluorinated vinyl monomers has started in 1982 to report many reactions to afford novel fluorinated polymers [1]. Radical polyaddition of bis(perfluoroisopropenyl) esters is another example of carbon–carbon bond formation which affords fluorinated polymers with organic compounds bearing carbon–hydrogen bonds by the precise radical shift mechanism [2]. The polymers obtained possess segments which have never been supposed to be incorporated into polymer main chains.

It is well-known that the fluorinated vinyl monomers are good acceptors for carbon radicals to form carbon–carbon bonds. High radical addition reactivity of fluorinated compounds such as tetrafluoroethylene, chlorotrifluoroethylene and perfluorocyclobutene onto ethers, alcohols and amines has been demonstrated by many research groups [3]. The high reactivity of perfluoroisopropenyl group has been reported in the reaction of 2-benzoxypentafluoropropene [CF_2=$C(CF_3)OCOC_6H_5$] (BPFP) with tetrahydrofuran (THF) to produce 1:1 addition compound (Eq. (1)). The reaction has been developed to yield fluorinated polymers from bis(1-trifluoromethyl-2,2-difluorovinyl) terephthalate [CF_2=$C(CF_3)$ $OCOC_6H_4COOC(CF_3)$=CF_2] (BFP) with 1,4-dioxane (DOX) bearing 9.9×10^3 as the highest molecular weight (Eq. (2)). The precise radical migration of the 1,5-shift mechanism is proposed in the reaction of BPFP with DOX, as shown in Scheme 1. The mutual repulsion between two fluorine atoms may sterically assist the mechanism of 1,5-radical transfer. The reaction has been confirmed to be applicable to a wide variety of fluorinated vinyl monomers with compounds bearing carbon–hydrogen bonds

[2]. The radical shift is similar to the chain transfer reaction with a solvent in a radical addition polymerization of nonfluorinated vinyl monomers. Typical nonfluorinated vinyl monomers such as styrene and methyl methacrylate produce the corresponding homopolymers under a radical condition and the chain transfer reaction may take place with solvents. High molecular weight polymers are generally produced since the chain transfer reaction rarely takes place with a solvent which shows likely poor hydrogen abstraction reactivity toward radicals at propagating chain ends.

$$(1)$$

$$(2)$$
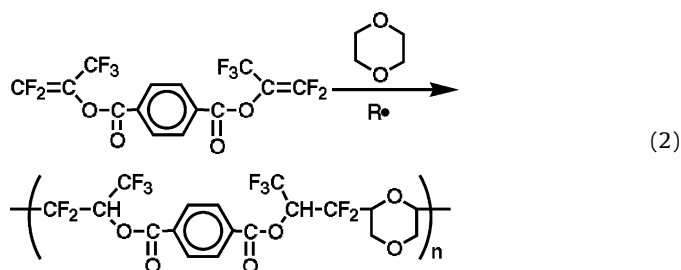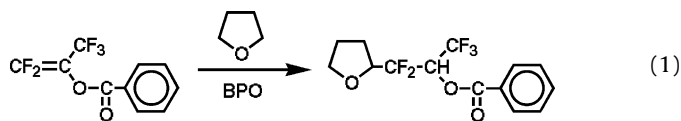
It is also confirmed that fluorinated vinyl monomers are a good acceptor of anionic species since the electron density of the vinyl group should be decreased to a considerable extent by the strong electron-withdrawing fluorine substituents although limited reports on anionic reactivity of fluorinated vinyl monomers have been available [1]. More detailed study on the anionic addition polymerization is desirable. Stereoregular fluorinated polymers may also be possible under anionic conditions. Anionic addition reactions of fluorinated vinyl monomers might be one of the candidates for preparation of carbon–carbon bonds. To repeat the carbon–carbon bond formation of anionic addition reactions, novel types of fluorinated polymers are expected to be yielded. No reports on the anionic polyaddition have been available. Polymers produced by the novel anionic polyaddition may possess groups which have never been supposed to be incorporated into polymer main chains.
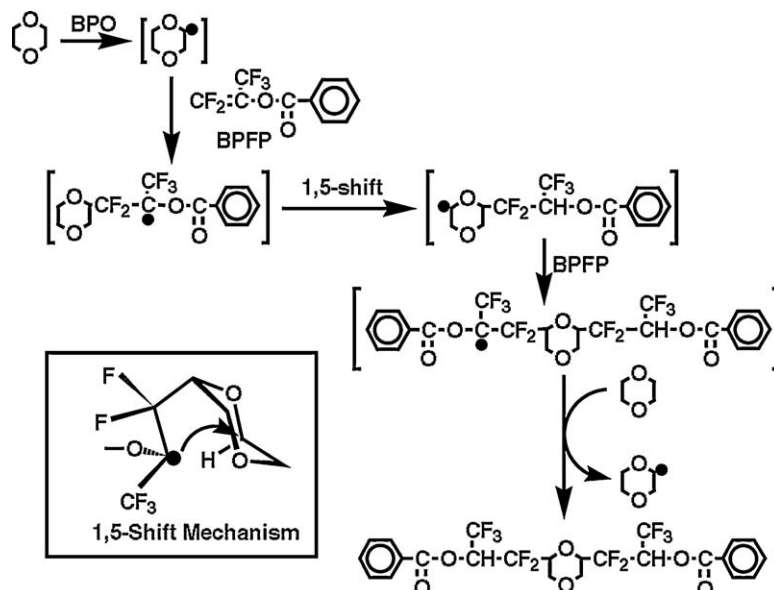
Scheme 1. Mechanism of the reaction of BPFP with DOX [2].

In this article recent development on facile carbon–carbon bond formation by the aid of fluorine-substituents under radical and anionic addition reaction conditions is introduced to afford novel fluoroalkyl compounds and new types of fluorinated polymers. Hydrocarbon analogues such as styrene and methyl methacrylate generally produce the corresponding homopolymers under radical or anionic reaction conditions. Gifts of serendipity were then presented such as γ-rays-induced polymerization and cationic polymerization on the way of investigation on the reactivity of fluorinated vinyl monomers developed by a novel concept.

The fundamental study on the reactions of fluorinated vinyl compounds has scarcely been carried out. Much information is available from patents because the development has mainly been accomplished by company research groups. It is important to knock on the door of the house of each fluorinated vinyl monomer to ask how the resident wants to act, and to accumulate the statements [1].

2. Radical addition and polyaddition

As has been described in the previous section, the high reactivity of BPFP as a radical acceptor affords addition products with organic compounds bearing carbon–hydrogen bonds [2]. The radical addition to BPFP is applicable to a wide variety of organic compounds bearing carbon–hydrogen bonds such as THF, DOX, 18-crown-6, hexanal, triethylamine, cycloalkanes and even hexane. The reaction is applicable to the formation of novel polymers when developed to bifunctional fluorinated vinyl compounds such as BFP. The polymers produced possess segments which have never been supposed to be incorporated into polymer main chains such as DOX, 18-crown-6, glutaraldehyde, triethylamine, and hexane. The investigation of the addition reaction with compounds which have never been examined previously has been developed to evolve radical addition and polyaddition reactions. Based on the reactions of monofunctional compounds to form carbon–carbon bonds, the radical polyaddition of bifunctional fluorinated vinyl compounds has also been examined.

Chain transfer reaction with solvent generally takes place when radical polymerization of typical hydrocarbon analogues such as styrene and methyl methacrylate is carried out in usual organic solvents bearing carbon–hydrogen bonds through hydrogen abstraction from solvent molecules. Low molecular weight oligomers are produced instead of high molecular weight polymers when the chain transfer reaction takes place frequently. The chain transfer reaction with solvents, however, rarely goes on. Reactivity of styrene or methyl methacrylate under radical conditions is high enough to overwhelm the chain transfer reaction in usual organic solvents to afford high molecular weight polymers. Introduction of functional groups at oligomer chain ends is possible when radical polymerization of nonfluorinated vinyl monomers is carried out in the presence of tetrachloromethane by applying chain transfer reaction with the chlorine abstraction.

2.1. Radical addition of 2-benzoxypentafluoropropene with carbonates

No report on the addition of fluorinated vinyl compounds to organic compounds possessing carbonyl compounds has been available. The additions of diethyl carbonate (DEC), dipropyl carbonate, ethyl methyl carbonate, dibenzyl carbonate and ethylene carbonate which possess two types of carbon–hydrogen bonds were examined [4]. The reaction of DEC with BPFP was carried out by reacting 107.8 mmol of DEC, 13.5 mmol of BPFP and 5.4 mmol of benzoyl peroxide (BPO) at 80 °C or of di-*tert*-butyl peroxide (DTBP) at 120 °C for 3 days. The conversion of BPFP was 53% for BPO and the isolated yield of the product was 15.5%. The reactivity of DEC is, hence, lower compared to those of THF or DOX since the conversions of BPFP were quantitative. The reaction was found to take place as shown in Eq. (3) by the results of NMR and GC-MS measurements of the product. The reaction takes place predominantly on the methylene group of DEC. DEC is mono-functional similar to THF.

$$(3)$$
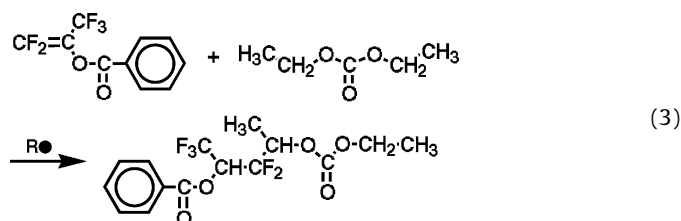
The results mentioned above indicate that the reaction takes place without the 1,7-radical shift mechanism, as shown in Scheme 2 [4], which is similar to that of the reaction of BPFP with THF. The mechanism of the hydrogen abstraction from diethyl
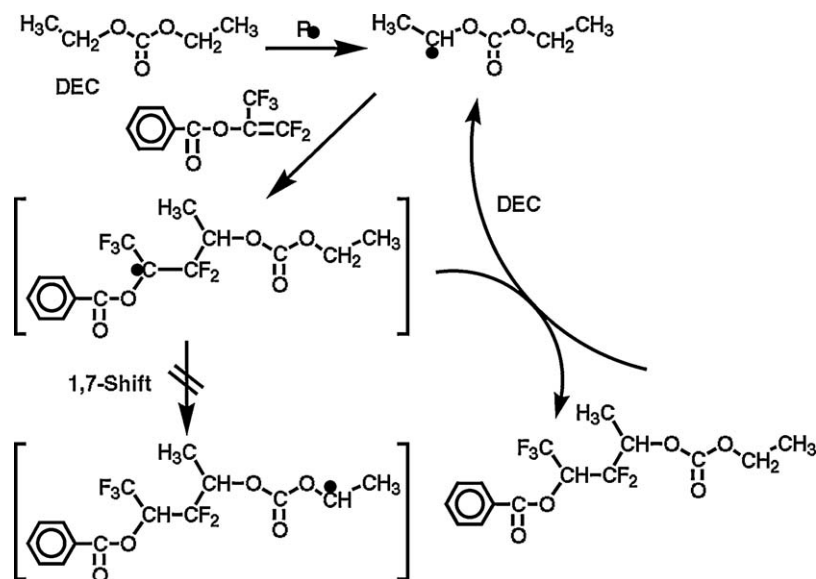
Scheme 2. Mechanism of the reaction of BPFP and DEC [4].

carbonate followed by the addition to BPFP is proposed. The radical is abstracted by DEC to form the DEC radical again instead of 1,7-radical shift followed by producing the di-addition compound of DEC. The reaction proceeds by this cycle.

The yield of addition product of BPFP to DEC initiated by DTBP was not obtained because a complex mixture was formed. The BPFP conversion of the radical reaction with dipropyl carbonate was quantitative. However, many products were detected by GC analyses. The reactions with ethyl methyl carbonate, dibenzyl carbonate and ethylene carbonate hardly took place because only a slight decrease of BPFP concentration was detected by GC.

This might be the first example which shows an addition of an organic compound bearing carbonyl group onto a polyfluorinated vinyl compound though isolated yield was rather low. Scarce chance to develop the reaction to preparation of polymers is demonstrated since carbonates perform basically as monofunctional compounds although carbonates possess many carbon–hydrogen bonds which might likely be attacked by radicals.

2.2. γ-Rays-induced polyaddition of bis(1-trifluoromethyl-2,2-difluorovinyl) terephthalate with ethers

As demonstrated previously [2,5] γ-rays-induced radical polyaddition of BFP with DOX was investigated since irradiation with γ-rays from a ^{60}Co source enables to generate radical species continuously, and it might be expected to produce higher molecular weight polymers compared to those yielded by a peroxide initiation. Prior to polyaddition, addition reactions of BPFP with THF and DOX, and BFP with THF were examined in order to confirm that the addition reaction may be applicable to preparation of polymers. The addition reaction of BFP with THF afforded the 1:1 and 1:2 addition products of BFP with THF by adding 1.5 mmol of BFP, 21.0 mmol of THF at 40 °C in vacuo. Only di-addition product of BFP was obtained by the irradiation of 60 and 100 kGy with quantitative yields. Then the addition reaction of the monofunctional BPFP with the difunctional DOX was investigated to preferentially afford 2:1 addition compound of DOX although the 1:1 addition product was also found to be produced. Tri-substituted dioxane bearing three BPFP moieties was not obtained. These results suggested the possibility of linear polymer syntheses by radiation-induced polyaddition of BFP with DOX. Polymers bearing molecular weights of about 1.5×10^4 were obtained under the feed molar ratio of DOX/BFP = 16 with an irradiation dose of 2000 kGy at 40 °C. ^{1}H, ^{13}C and ^{19}F NMR spectra showed that the polymer possessed BFP units and DOX units in the main chain by about 1:1 ratio. The TGA result showed that the 5% weight-loss temperature was about 329 °C.

More detailed study on the radiation-induced polyaddition of BFP with DOX and optimization of the reaction conditions was carried out [6]. It was necessary to irradiate with doses of 2000, 1500 and 750 kGy to obtain the quantitative conversion of BFP at the feed molar ratios DOX/BFP = 8.0, 16, and 32, respectively. The step-growth polymerization mechanism was suggested by measurements of molecular weights of the polymers obtained with several irradiation doses because of the increase of the molecular weights and the broadening of the molecular weight distribution of the polymers caused by the increase of irradiation dose at the late stage of polymerization. The steep increase of molecular weight was observed at the feed molar ratio of DOX/BFP of 8.0 with the irradiation doses above 2000 kGy and the polymer with the weight-average molecular weight of 2.4×10^4 was obtained with the dose of 3000 kGy under quantitative conversions of BFP. The reaction between polymers might then take place after the quantitative conversion of BFP. The polymer might be applicable to an anti-radiation material since the polymer was produced with the irradiation doses at as high as 3000 kGy without remarkable degradation.

The γ-rays irradiation-induced radical polyaddition of BFP was examined in the presence of an excess of cyclic and acyclic ethers in feed at 0 °C [7]. The irradiation of BFP with an 8-fold excess of DOX and diethyl ether (EE) gave unimodal polymers consisting of the alternating unit of BFP and DOX moieties (poly(BFP-alt-DOX), $\overline{M}_{n,as-prepared} = 5.1 \times 10^3$) and of BFP and EE (poly(BFP-alt-EE), $\overline{M}_{n,as-prepared} = 3.9 \times 10^3$), respectively, without a remarkable side reaction. The irradiation of BFP with an 8-fold excess of THF or tetrahydropyran (THP) provided only the 1:2 addition product in high yields. Monofunctional BPFP as a model compound showed preferential formation of the 2:1 adduct to the 1:1 adduct with DOX and EE.

The kinetic analysis of the model reactions revealed that the rate constants for the formation of the 2:1 adducts (k_d) of BPFP with DOX and EE were 3.1×10^9 M^{-1} s^{-1} and 7.1×10^9 M^{-1} s^{-1}, respectively, where the ratio of rate constants (k_d/k_m) for the formation of the 2:1 adducts, k_d, and the 1:1 adducts, k_m, were 120 and 450, respectively. 2 Orders of magnitude higher k_d than k_m indicated that the addition reaction of ethereal radicals at the polymer chain ends produced by the addition of ethereal radicals to perfluoroisopropenyl groups followed by the intramolecular hydrogen abstraction takes place with another BFP preferentially compared to intermolecular radical transfer with excess ethers. Then the propagation reaction of the intermediate bearing perfluoroisopropenyl moieties at both ends of the molecule takes place even in the circumstance of the excess amount of ethers in the reaction systems to give polymers such as poly(BFP-alt-DOX) and poly(BFP-alt-EE). The polyaddition of BFP with DOX, which has the lower reactivity and the lower rate constant ratio of k_d/k_m compared to those of EE, provided higher molecular weight polymers. It is obvious that radiation-induced step-growth polymerization requires a high rate constant ratio of k_d/k_m as well as high radiation resistance to form high molecular weight polymers [7].

2.3. Radical addition of tris(1-trifluoromethyl-2,2-difluorovinyl) 1,3,5-benzenetricarboxylate with diethoxydimethylsilane

Crown ether moiety is incorporated into polymer main chain in the presence of BPO as a radical generator by the reaction of BFP with 18-crown-6. It is interesting to obtain a soluble polymer directly from a crown ether as a starting reagent although 18-crown-6 possesses 24 carbon–hydrogen bonds which are likely to be attacked. It might be one of the reason why the soluble polymers are yielded from crown ether that the controlled intramolecular radical shift such as 1,5-shift or 1,6-shift mechanism would take place precisely during the polyaddition reaction [2]. By hydrolyses of polymers obtained with precise radical shift, novel fluorinated organic compounds such as di-fluoroalkylated 18-crown-6 might be yielded. Several 18-crown-6 derivatives were produced including mono-, di- and tri-substituted 18-crown-6 when reacted with BPFP. An organic synthesis through polymerization reactions would be possible, which are discussed in the following section. Fluorinated hybrid polymers possessing alkylsilyl groups in main chain were also prepared from BFP with diethoxydimethylsilane (DEOMS) [8].

It is then interesting to investigate a radical addition reaction of a compound possessing three perfluoroisopropenyl groups with difunctional ethers [9]. Tris(1-trifluoromethyl-2,2-difluorovinyl) 1,3,5-benzenetricarboxylate [$C_6H_3(COOC(CF_3)=CF_2)_3$] (TFM) was synthesized from 1,3,5-benzenetricarbonyl trichloride with 3 eq. of lithium enolate derived from 1,1,1,3,3,3-hexafluoroisopropanol and 2 eq. of butyllithium. 1,3,5-Benzenetricarbonyl trichloride was synthesized by the reaction of 1,3,5-benzenetricarboxylic acid with phthaloyl dichloride supplied by Iharanikkei Co. Usual chlorination agents such as thionyl chloride or phosphorous

trichloride did not work well to produce 1,3,5-benzenetricar-boxylic acid anhydride instead of the acid chloride.

To estimate the radical addition reactivity, the reaction of TFM (5.0 eq.) with THF (40 eq.) was examined in the presence of BPO at 80 °C or DTBP (2.0 eq.) at 120 °C for 3 days. The quantitative conversions of TFM were observed. The main product was the 1:3 addition compound of TFM with THF. The peak assignable to the 1:1 addition compound of TFM with THF was also detected in low yields in the GC measurement. The reaction time dependency on the conversion of TFM with THF was examined in the presence of BPO at 80 °C to afford the results that the radical addition reactivity of TFM was as high as that of BPFP since the conversions of TFM were 86% at 15 min and 97% at 120 min compared to the conversions of BPFP of 98% at 15 min and 100% at 120 min. The results of the model reaction of TFM with THF pointed out that the polyaddition of TFM with difunctional ethers might be possible if reaction conditions were properly set up although a cross-linked polymer might be yielded by the polyaddition of trifunctional TFM with a difunctional ether because of the production of tri-addition compound of TFM with THF.

The highest molecular weight polymer of 1.1×10^4 as the number-average molecular weight was obtained by the reaction of 5.0 eq. of TFM with 120 eq. of DEOMS initiated by DTBP as a radical generator at 120 °C though the yield of the polymer was 1.0%, probably because low molecular weight oligomers might be soluble in reprecipitation solvent such as methanol. The composition of the TFM moiety and DEOMS moiety in the polymer obtained was approximately 1:1 determined by the area ratio of ^{1}H NMR. The results suggested that the reaction might take place at methylene carbon of DEOMS as shown in Eq. (4), as reported in the polymerization of BFP with DEOMS. Higher concentration of DTBP added in reaction systems achieved gelation probably because of

the higher hydrogen abstraction ability. Difluoromethylene group (–CF$_2$–) in the reaction intermediate may assist the 1,5-radical migration because of the mutual repulsion between two fluorine atoms cited in Scheme 1.

(4)
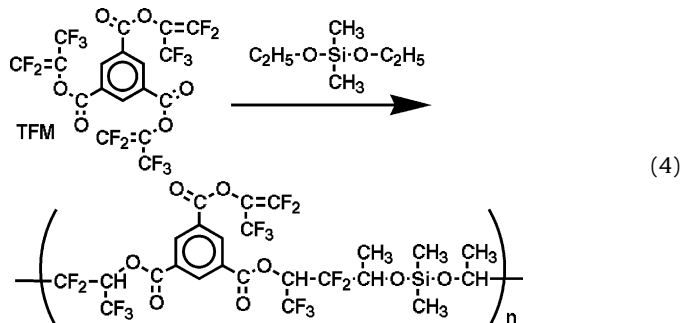
Postulated polyaddition mechanism is shown in Scheme 3 [9]. The addition reaction of the hydrocarbon radical yielded by the hydrogen abstraction would take place to generate the trifluoromethyl-substituted carbon radical. The 1,7-radical shift may take place to yield the hydrocarbon radical again followed by the addition of TFM to produce the trifluoromethyl-substituted carbon radical again. The precise 1,7-radical shift might make it possible to incorporate polyfunctional compounds into the polymer main chain. The mechanism suggests that the more detailed study on the polymerization condition would give polymers possessing higher molecular weight fluorinated hybrid polymers in higher yields. The polymer obtained might perform as a functional fluorinated hybrid polymer which possesses many perfluoroisopropenyl groups in side chains and alkylsilyl groups in main chains.
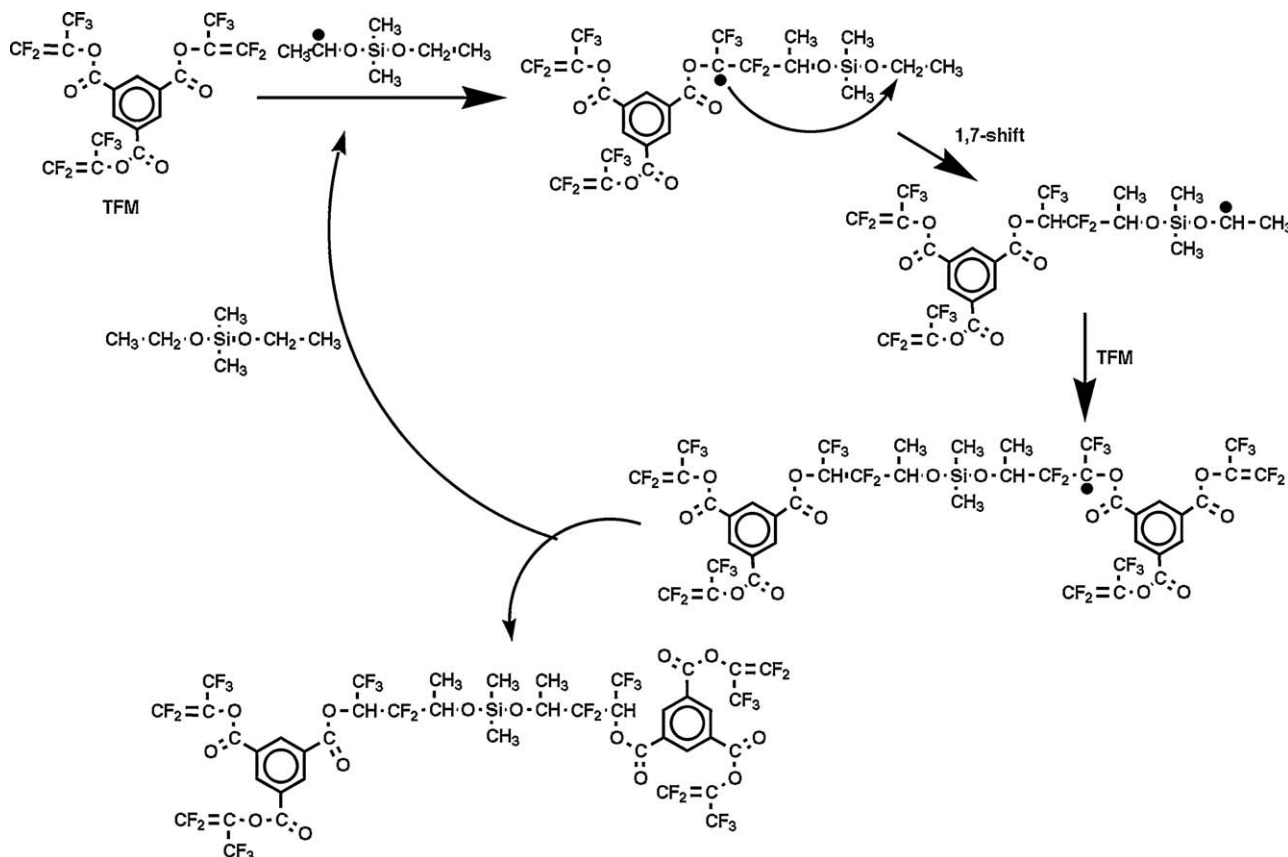

Scheme 3. Polyaddition mechanism of TFM with DEOMS [9].

Similar results were obtained by the polyaddition of trifunctional TFM with multifunctional 18-crown-6. The molecular weight of hexane insoluble part was about 3×10^3.

2.4. Allyl polymerization of 4-pentenoyloxypentafluoropropene

As has been demonstrated, the cyclopolymerization of perfluoroisopropenyl vinylacetate $[CH_2=CH–CH_2–COOC(CF_3)=CF_2]$ takes place under radical polymerization condition to produce the polymer possessing 5-membered-ring structure in main chain (Eq. (5)) although it is well-known that the homopolymerization reactivity of allyl group and perfluoroisopropenyl group is quite poor. It would then be attractive to synthesize a polymer possessing 6-membered-ring structure in main chain. The novel fluorinated vinyl compound, 4-pentenoyloxypentafluoropropene $[CH_2=CH–(CH_2)_2–COOC(CF_3)=CF_2]$ (PPF) which has one more methylene carbon compared to perfluoroisopropenyl vinylacetate, was synthesized and the polymerization reactivity was examined [10].

$$(5)$$
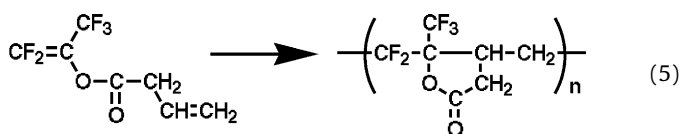
Polymers of highly viscous liquids were obtained with the reprecipitation by methanol and hardly separated by filtration. A high molecular weight polymer of 1.8×10^4 as a number-average molecular weight was obtained by the initiation with DTBP at 100 °C for 3 days. Results of analyses by ^1H, ^{13}C and ^{19}F NMR measurement showed the conclusion that the vinyl polymerization of allyl groups took place instead of the cyclopolymerization yielding the 6-membered-ring structure (Eq. (6)). The radical polymerization of PPF with BPO might be initiated by phenyl or benzoxy radical addition since small peaks assignable to phenyl protons were detected. The degree of polymerization ($\overline{DP}$) derived from the area ratio of phenyl protons to methylene protons in ^1H NMR was about 23, which might agree with about 38 as a ($\overline{DP}$) calculated from size-exclusion chromatographic measurement when the termination may take place by radical recombination reaction.

$$(6)$$
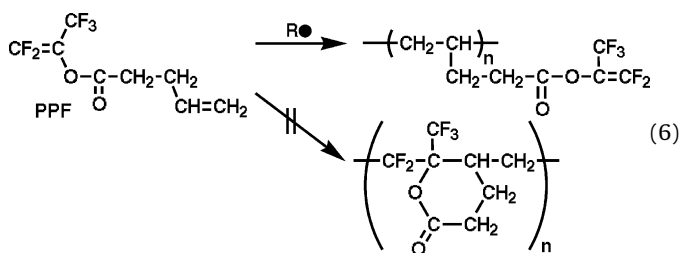
The polymerization reactivity of the allyl group in PPF is concluded to be high enough to yield polymers by the vinyl polymerization. The radical polymerization of an allyl group in hydrocarbon analogue is well-known to produce low-molecular weight oligomers because of the degradable chain transfer during the propagation reaction. The cyclopolymerization of diallyl compounds has been reported by several research groups. The cyclopolymerization of perfluorinated α,ω-divinyl compounds is accomplished by research groups of Asahi Glass Company and duPont Company. The reason why the polymerization reactivity of the allyl group in PPF is extraordinary high might be because of the presence of perfluoroisopropenyl group which may influence the stability of the radical at the propagating chain end to be protected from degradable chain transfer.

Other functional groups may be introduced into perfluoroisopropenyl groups as side groups in polymers with a wide variety of organic compounds possessing carbon–hydrogen bonds by developing the addition of BPFP with cyclic ethers and alcohols. This may be a gift from serendipity.

## 2.5. Radical addition of heptafluoropropyl trifluorovinyl ether

Radical addition reactions of alcohols, ethers and amines to polyfluorinated vinyl compounds such as tetrafluoroethylene, chlorotrifluoroethylene and perfluorocyclobutene have been reported by many research groups [3]. The reactions were initiated by radicals or γ-rays irradiation although the polymerization of tetrafluoroethylene and chlorotrifluoroethylene took place simultaneously. The section concerns the addition of cyclic ethers such as THF, THP, DOX and 1,3-dioxolane (DL) to heptafluoropropyl trifluorovinyl ether $[CF_2=CF–O–C_3F_7]$ (PPVE) [11].

The addition reactions of cyclic ethers on PPVE were carried out by adding 5 eq. of PPVE and 40 eq. of the cyclic ether in the presence of 2 eq. of BPO at 60 °C for 3 days. The conversions of PPVE were quantitative under these reaction conditions. The reactivity of PPVE was, then, as high as that of BPFP since the conversions of BPFP were also quantitative in the reaction of THF and DOX systems. GC-MS measurements indicated the production of 1:1 addition compounds of PPVE with THF. A trace amount of the 2:1 adduct appeared in GC. Thus, THF behaves as a monofunctional compound. The isolated yield of the 1:1 addition product was 75% as a 1:1 mixture of diastereoisomers. The analyses showed that the addition reaction took place at the position 2 of THF.

The reaction of PPVE with THP showed a similar GC pattern compared to that of the THF reaction system. No peaks assignable to the 2:1 addition product of PPVE and THP were observed in GC. Hence, THP also performs as a monofunctional compound. The isolated yield of the 1:1 addition product was 79% as a 1:1 mixture of diastereoisomers with a trace amount of regioisomer. The analyses of the main product demonstrated that the addition reaction took place at the position 2 of THP.

GC of the reaction mixture of PPVE with DOX showed large peaks assignable to the 1:1 adduct and small peaks assigned to the 2:1 adduct. The area ratio of these two peaks was about 8:2. The isolated yield of the 1:1 addition product was 68% as a 1:1 mixture of diastereomers. DOX, therefore, performs mainly as a monofunctional compound. The radical addition mechanism shown in Scheme 4 [11] is similar to that of BPFP with DOX, wherein the benzoxy radical generated from BPO abstracts a hydrogen at the position 2 of DOX followed by the addition onto PPVE to form the radical at the α-position of the PPVE moiety. The 80% of the radical abstracts a hydrogen from DOX to yield the radical at the position 2 of DOX again to afford the 1:1 addition product. The 20% of the residual radicals might migrate intramolecularly by the 1,5-shift mechanism to the position 6 of the DOX moiety in the intermediate and the addition of the radical takes place onto PPVE again to form the radical at the α-position of the PPVE moiety to yield the 1,6-disubstituted DOX derivative. The reaction of BPFP with DOX, as has been mentioned in the beginning of the article, afforded preferentially the 2,6-disubstituted DOX through 1,5-radical shift mechanism. It is suggested that the effect of trifluoromethyl-substituted carbon radical yielded by the reaction of BPFP with DOX might be different from that of the monofluorocarbon radical produced by the reaction of PPVE with DOX. The assistance of the mutual repulsion between two fluorine atoms in the reaction of PPVE with DOX might be lower compared to that of the reaction of BPFP with DOX because of the absence of trifluoromethyl group.

The reaction of PPVE with DL showed a similar GC pattern compared to that of PPVE with THP. No peaks assignable to the 2:1 addition product of PPVE with DL was shown in GC and GC-MS. DL thus behaves as a monofunctional compound. The isolated yield of the 1:1 adduct was 57% and contained trace amount of
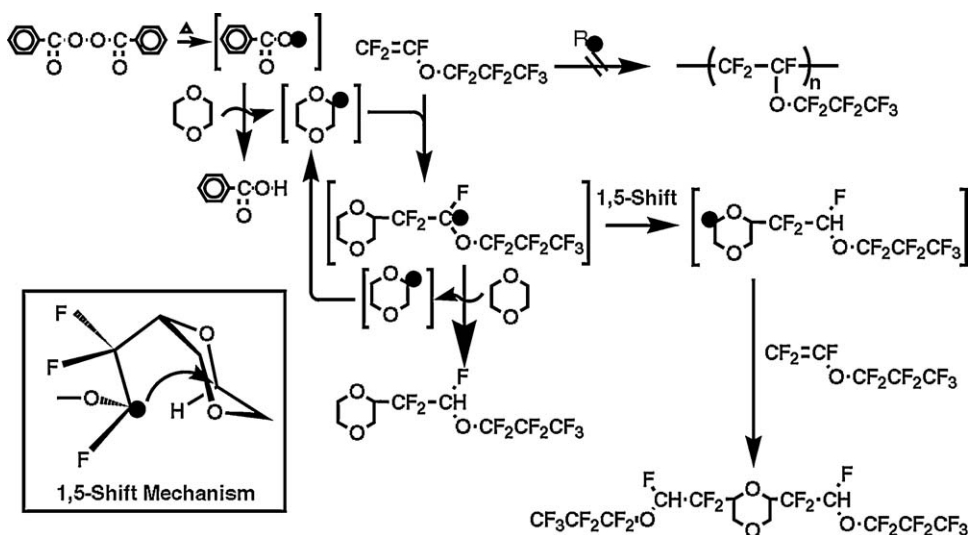
Scheme 4. Mechanism of the reaction of PPVE with DOX [11].

regioisomers. The analyses demonstrated that the addition reaction took place at the position 2 of DL.

The method presents a facile method of preparation of cyclic ethers possessing fluoroalkyl substituents. The reaction may scarcely be applicable to preparation of polymers by the radical polyaddition since yields of the 2:1 addition products of PPVE with cyclic ethers are poor. It may, however, be probable that the polyaddition of a perfluorinated α,ω-divinyl compound with DOX would achieve a production of polymers under appropriate reaction conditions since DOX afforded the 1:2 addition compound with PPVE though the yield of the di-addition product was rather low.

### 2.6. Radical addition of 2-trifluoromethylacrylate with cyclic ether

It is interesting how many fluorines should then be necessary for the interconversion of fluoroalkylcarbon radicals and hydrocarbon radicals in the reaction intermediates in the addition reactions since tetrafluoroethylene, chlorotrifluoroethylene and BPFP yielded the corresponding addition products. It may afford some information on how many fluorines might be needed for radical addition toward ethereal compounds to investigate the radical addition reactions of α-trifluoromethylacrylate. Radical reactions of acrylates and vinyl esters possessing no fluorine atom generally produce polymers instead of addition products. The radical additions of ethyl β-fluoroacrylate with THF and DL have been reported to afford the corresponding addition products achieving carbon–carbon bond formation which demonstrated that β-monofluorinated acrylate achieved the addition onto ethereal compounds in spite of its high radical polymerization reactivity. The addition of *tert*-butyl 2-trifluoromethylacrylate [CH$_2$=C(CF$_3$)COOC(CH$_3$)$_3$] (BFMA) supplied by Tosoh F-Tech Inc with THF, DOX, DL and THP in the presence of 2,2′-azobisisobutyronitrile (AIBN), BPO or DTBP was investigated [12].

The reaction of BFMA with THF was carried out by adding 1.5 mmol (5 eq.) of BFMA and 12.0 mmol (40 eq.) of THF in the presence of 0.6 mmol (2 eq.) of AIBN at 60 °C, BPO at 80 °C or DTBP at 120 °C for 3 days. The conversions of BFMA were above 99% by GC measurements of the reaction systems. The product was 2-substituted THF as shown in Eq. (7). The isolated yields of the product were 69% initiated with AIBN, 54% with BPO and 16% with DTBP, respectively, after distillation. THF is monofunctional since no apparent peak assignable to the di-addition product of THF was detected in the GC. ^{1}H-^{1}H COSY and ^{1}H-^{13}C HMQC NMR results also indicated that the product was the mixture of diastereoisomers.

BFMA was found to show much higher reactivity compared to that of BPFP since BFMA was consumed over 90% within 1 min and the conversion of BPFP was about 70% in 15 min. It may be concluded that the ability of the trifluoromethylvinyl group as a radical acceptor is higher than that of the perfluoroisopropenyl group.

(7)
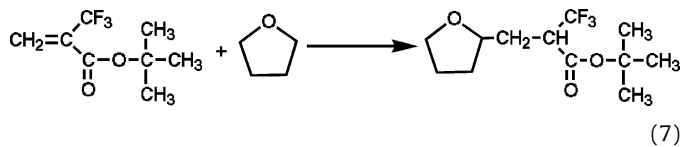
The reaction of 18.0 mmol (5 eq.) of BFMA with 144 mmol (40 eq.) of DL in the presence of 7.2 mmol (2 eq.) of BPO at 80 °C for 3 days was carried out to afford the quantitative conversion of BFMA with 63% as an isolated yield of the 1:1 addition product. The results of the analyses supported the reaction as shown in Eq. (8).

(8)
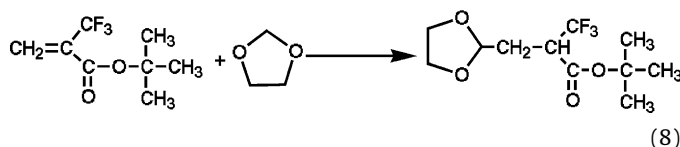
Radical additions of BFMA with DOX and THP were also examined to afford the corresponding 1:1 addition products in fairly high yields by achieving carbon–carbon bond formation as shown in Eqs. (9) and (10). It is interesting that no 2,6-disubstituted DOX was detected in the GC. No 1,5-radical shift mechanism might, therefore, take place in the case of BFMA with DOX, probably because the reactivity of the radical •C(CF$_3$)(COOC(CH$_3$)$_3$)CH$_2$– would be different from that of the radical •C(CF$_3$)(OCOC$_6$H$_5$)CF$_2$–. It is then concluded that the 1,5-radical shift of the trifluoromethyl-substituted carbon radical to produce a hydrocarbon radical may not take place in the reaction intermediate of BFMA which possesses two less fluorines compared to BPFP. It may be another reason that there is no assist of the repulsive force of two fluorine atoms to the 1,5-radical shift in the cyclized mechanism in the reaction of BFMA with DOX.

(9)

$$(10)$$
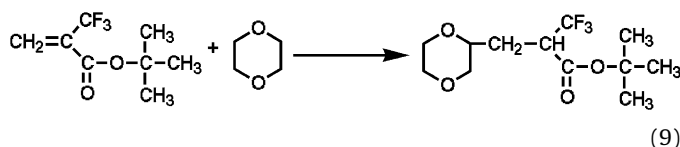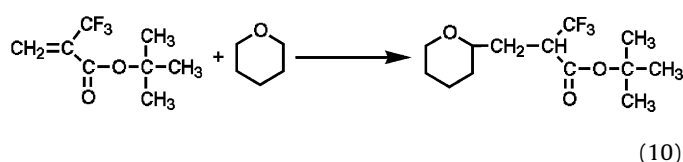
The reaction may open a useful road to utilize compounds of a low polymerization reactivity for the preparation of organic compounds although a scarce chance to develop the reaction to the preparation of polymers by the polyaddition is demonstrated since DOX performs basically as a monofunctional compound.

2.7. Synthesis and polymerization of novel bis(2-trifluoromethylacrylate)
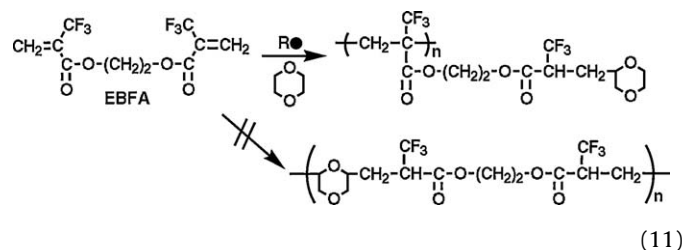
As has been reported previously, the scarce polymerization reactivity of 2-trifluoromethylacrylate derivatives is demonstrated under radical polymerization conditions, and high yields of 2-trifluoromethylacrylate polymers are obtained under anionic conditions [1]. High radical addition reactivity of BFMA has been proved in the previous section. BFP shows the high radical polyaddition reactivity to form polymers with DOX, as has been demonstrated in previous section. Then radical polyaddition of a novel bis(2-trifluoromethylacrylate), ethylene bis(2-trifluoro-methylacrylate) [$CH_2=C(CF_3)COOCH_2CH_2OCOC(CF_3)=CH_2$] (EBFA), was of interest [13].

EBFA was synthesized by the reactions of 2-trifluoromethy-lacryloyl chloride with ethylene glycol in the presence of triethylamine as a hydrogen chloride acceptor to afford the EBFA in fairy high yields. The radical addition of ethyl 2-trifluoromethylacrylate with DOX yielded mainly the 1:1 addition product and the 2:1 adduct only 9% in the analysis of GC area ratios. The radical polyaddition reaction with DOX was still examined although the results of the model reaction suggested that the scarce polyaddition of EBFA with DOX yields polymers possessing DOX moieties in main chain. A gel formation was observed by the addition of less amount of DOX into the reaction systems. 60 Eq. or more DOX with 5 eq. of EBFA was needed to obtain soluble polymers initiated with BPO. High molecular weight polymers as high as 5.6×10^4 were yielded by the addition of a larger amount of initiator. By the analyses with NMR measurements of the polymer obtained, no signals assigned to $CH_2=$ protons were observed and the polymer possessed monosubstituted DOX moieties. These results demonstrated that the vinyl polymerization of 2-trifluoromethylacrylate took place with the radical addition of DOX at the pendant 2-trifluoro-methylacrylate group quantitatively as shown in Eq. (11) instead of yielding polymers bearing DOX moieties in the polymer main chain by the radical polyaddition. It might be a new finding that the addition polymerization of the 2-trifluoromethylacrylate group takes place under the radical reaction condition to afford high molecular-weight polymers although low molecular-weight oligomers of methyl 2-trifluoromethylacrylate have previously been reported to be produced in low yields. This may be ascribable to large substituents of propagating chain ends to stabilize propagating radicals which would be protected from termination and chain transfer reactions. This demonstrates another new fashion of the polymerization of 2-trifluoromethy-lacrylate derivatives. The conclusion is far from that of the reaction of BFMA with DOX mentioned in the previous section. More detailed investigation should be needed on the mechanism of the addition polymerization accompanied by the radical addition.

$$(11)$$

The 5% weight-loss temperature of the polymer of EBFA with DOX was 309 °C as measured by TGA.

2.8. Syntheses and polymerization of novel fluoroalkyl methacrylates and 2-trifluoromethylacrylates

As has been reported previously, the radical addition reaction of BPFP with a wide variety of organic compounds bearing carbon–hydrogen bonds affords mono-addition products accomplished by the carbon–carbon bond formation. Fluorinated vinyl compounds are possibly candidates for the preparation of fluorinated organic compounds. Fluorinated alcohols might, for example, be acquired by the reaction of BPFP with ethanol or 2-propanol. Fluorinated alcohols would also be obtained by the hydrolyses of the compounds derived from BPFP with cyclic ethers such as THF,
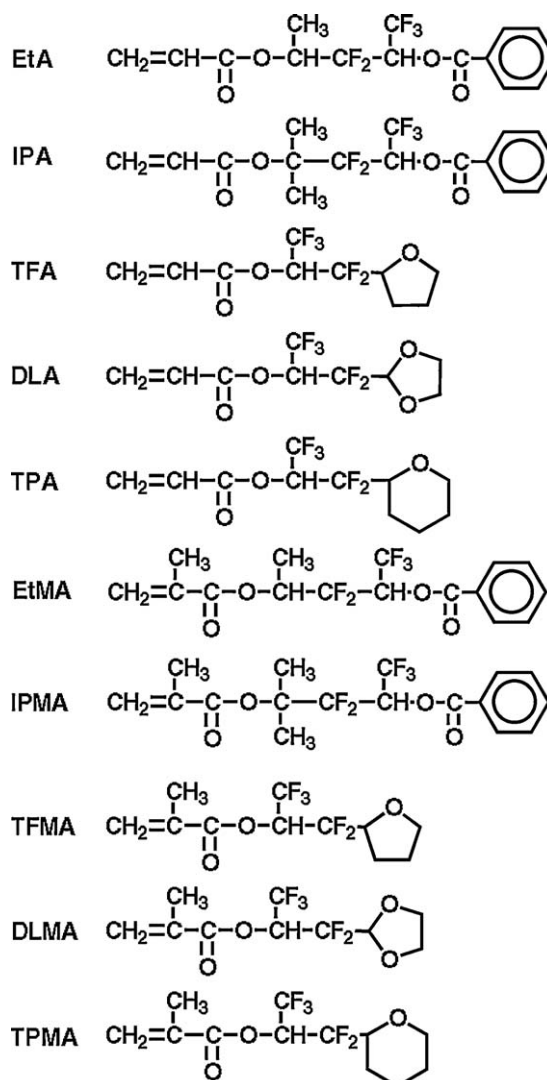
Scheme 5. Monomers appeared in Table 1 [14].

DOX, DL and THP. Novel fluoroalkyl acrylates and methacrylates bearing cyclic structures would be yielded by the reactions of these fluorinated alcohols with acryloyl or methacryloyl chlorides [14]. Acrylate and methacrylate polymers possessing fluoroalkyl groups bearing cyclic structures might be applicable to photoresist lithography.

BPFP afforded addition products with ethanol and 2-propanol in the yields of 65% and 69%, respectively. BPFP with THF, DL and THP also gave the corresponding mono-addition compounds in the isolated yields of 87%, 56%, and 55%, respectively. Hydrolyses of these mono-addition compounds were achieved by adding sodium hydroxide in methanol to yield the corresponding fluorinated alcohols in good yields. Novel fluoroalkyl acrylates and methacrylates synthesized are shown in Scheme 5 [14]. Radical polymerization of these fluoroalkyl acrylates and methacrylates yielded polymers of 1.2×10^5 as the highest molecular weight initiated with BPO or AIBN in fairy high yields, as shown in Table 1 [14].

The reaction was applicable to syntheses of fluoroalkyl 2-trifluoromethylacrylate derivatives possessing cyclic structures in ester groups. Syntheses of 2-trifluoromethylacrylate derivatives examined recently are schematically depicted in Scheme 6 [15]. The summary of anionic and radical polymerization reactivities of 2-trifluoromethylacrylates bearing THF or DL moieties is shown in Table 2. It is clearly demonstrated that these monomers produce high molecular-weight polymers under anionic and radical conditions although 2-trifluoromethylacrylates possessing small alkyl groups as ester alkyls yield scarcely high polymers under radical conditions. This may be another example of the high polymerization of 2-trifluoromethylacrylates. A polymer of 2-trifluoromethyl acrylates possessing fluoroalkyl group bearing cyclic structures might also be applicable to photoresist lithography.

2.9. γ-Rays-induced polymerization of heptafluoropropyl trifluorovinyl ether

On the way of the investigation on the radical addition of PPVE with cyclic ethers, the polymerization under γ-rays irradiation was examined since no report on the homopolymerization of PPVE has been available. The polymerization reactivity of polyfluorinated vinyl monomers is extremely low except few compounds such as tetrafluoroethylene and chlorotrifluoroethylene under radical conditions and hexafluoro-1,3-butadiene under an anionic condition. Then copolymerization with other vinyl compounds has ever been examined and many reports on alternating copolymers of polyfluorinated vinyl monomers with nonfluorinated ones have been published. PPVE was in the similar situation. The study has started on the investigation of producing alternating copolymer of PPVE with hexafluoroacetone under a radical condition. All attempts finished in vain as far as yielding alternating copolymer was concerned. In the course of the study the γ-rays-induced reaction showed the decrease of PPVE monomer to yield highly

Table 1
Radical polymerization of fluorine-containing acrylates and methacrylates [14].

Run	Monomer[a]	Initiator[b]	Solv.	Yield (%)	$\overline{M}_n$ ($\times 10^5$)[c]	$\overline{M}_w/\overline{M}_n$[c]
1	EtA	BPO		30	0.31	2.1
2		AIBN		39	0.66	2.7
3		AIBN	Tol.	45	0.10	1.3
4	IPA	BPO		76	0.34	9.0
5		AIBN		46	1.24	3.2
6		AIBN	Tol.	40	0.11	1.4
7	TFA	BPO		–	0.01	–
8		AIBN		34	0.08	6.9
9		AIBN	Tol.	0	–	–
10	DLA	BPO		gel	–	–
11		BPO	Tol.	62	0.06	–
12		AIBN		gel	–	–
13		AIBN	Tol.	66	0.08	–
14	TPA	BPO		gel	–	–
15		AIBN		48	0.45	2.2
16	EtMA	BPO		11	0.69	3.9
17		BPO	Tol.	47	0.12	2.0
18		AIBN		0	–	–
19	IPMA	BPO		66	0.82	4.1
20		BPO	Tol.	61	0.74	2.2
21		AIBN		67	0.53	2.6
22	TFMA	BPO		48	0.85	4.3
23		AIBN		73	0.46	2.1
24		AIBN	Tol.	14	0.23	2.7
25	DLMA	BPO		49	0.05	–
26		AIBN		45	0.17	–
27		AIBN	Tol.	54	0.51	1.3
28	TPMA	BPO		70	0.68	6.2
29		BPO	Tol.	0	–	–
30		AIBN		15	0.11	1.6

[a] See Scheme 5.
[b] Reaction temperature: AIBN 60 °C; BPO 80 °C.
[c] Estimated by SEC(PSt standards, eluent: THF).

Scheme 6. Synthesis of novel 2-trifluoromethylacrylates [15].

Table 2
Polymerization reactivity of 2-trifluoromethylacrylate.

Run	Monomer	Initiator	Yield (%)	$\overline{M}_n \times 10^4$	Ref.
1	$CH_2=C(CF_3)COOCH_3$	*tert*-BuOK	92		[a]
2		Radical	0		[b]
3	$CH_2=C(CF_3)COOCH_2CF_3$	$LiZnBuEt_2$	69		[c]
4		BPO	tr	0.3	[d]
5	$CH_2=C(CF_3)COOC(CH_3)_3$	Anion	0		[d]
6		AIBN	tr	0.2	[d]
7	$CH_2=C(CF_3)COOCH(CF_3)CF_2(C_4H_7O)$	$LiZnBuEt_2$	90	0.2	[e]
8		BPO	3	1.1	[e]
9	$CH_2=C(CF_3)COOCH_2CH(CF_3)CH_2(C_4H_7O)$	$LiZnBuEt_2$	tr	0.2	[d]
10		AIBN	2	1.0	[d]
11	$CH_2=C(CF_3)COOCH_2CH(CF_3)CH_2(C_3H_5O_2)$	$LiAlBuEt_3$	tr	0.6	[d]
12		BPO	2.5	1.6	[d]
13	$CF_2=C(CF_3)OCOC_6H_5$	Anion	0		[f]
14		Radical	0		[f]

[a] Narita, T.; Hagiwara, T.; Hamana, H.; Nara, T. Makromol. Chem., Rapid Commun., 1985, 6, 301.
[b] Ito, H.; Miller, D. C.; Willson, C. G. Macromolecules, 1982, 15, 915.
[c] Narita, T.; Hagiwara, T.; Hamana, H.; Maesaka, S. Polym. J., 1988, 20, 519.
[d] Unpublished data.
[e] [15].
[f] [2].

viscous oil like pine resin [16]. The irradiation of PPVE under γ-rays from ^{60}Co was then examined since the continuous formation of radicals is well-known to take place under the γ-rays irradiation on organic compounds. The conversion of PPVE was found to be increased with the increase of the irradiation dose and yields of the products were also elevated. The product was insoluble in usual organic solvents and partly soluble in hexafluorobenzene. The analyses were then restricted. The 5% weight-loss temperature (T_{d5}) was 144 °C for the polymer produced at 250 kGy, 169 °C at 500 kGy, and 165 °C at 1000 kGy, respectively. The T_{d5} might be roughly related to molecular weight of polymers. It is confirmed that the T_{d5}'s of the polymers yielded up to 1000 kGy were elevated. The results suggested that the increase of molecular weight of the polymers would presumably take place. The higher dose of irradiation over 1000 kGy showed the results of decreasing T_{d5}, 156 °C at 2000 kGy, 144 °C at 3000 kGy, and 130 °C at 7400 kGy, respectively; which suggested a low molecular-weight product formation or a degradation of yielded polymers. Measurement of viscosity of the hexafluorobenzene-soluble part yielded at 2000 kGy irradiation showed as high as [η] = 0.47. The homopolymer of PPVE was concluded to be produced under the irradiation of γ-rays. The results of ^{13}C-NMR and diffusion reflection infrared spectral measurements of hexafluorobenzene-soluble part of the product supported that the homopolymerization of vinyl groups would take place. This may be a gift of serendipity as the study on the polymerization of perfluorovinyl compound was attempted enthusiastically.

2.10. Organic synthesis through polymerization reaction

As has been demonstrated previously, a polymer bearing a controlled structure is obtained by the precise radical shift mechanism such as the reactions of BFP with DOX and BFP with diethoxydimethylsilane through the carbon–carbon bond formation [2]. Polymers produced by the radical polyaddition would then be starting materials for syntheses of novel organic compounds. Novel fluorinated organic compounds which would be impossible to be synthesized by usual methods might be yielded by hydrolyses of the polymers since new carbon–carbon bond formation reactions are achieved. An organic synthesis through polymerization reaction may be practicable because of the precise radical transfer accompanied by carbon–carbon bond formation.

The hydrolyses of the polymer obtained by the reaction of BFP with tetraethoxysilane, for example, were summarized by Eq. (12)

[17]. The fluorine-containing product of the hydrochloric acid catalyzed hydrolysis might be difficult to be synthesized by usual methods. The di-addition product of 18-crown-6 may be obtained by the hydrolysis of the polymer yielded by the radical polyaddition of BFP with 18-crown-6 since several products including tri- and tetra-substituted 18-crown-6 derivatives were yielded by the reaction of BPFP with 18-crown-6 (Eq. (13)) [18].

$$(12)$$

$$(13)$$
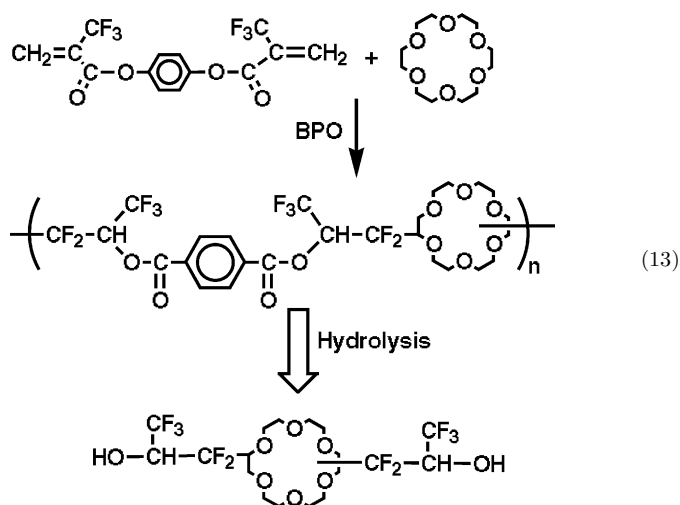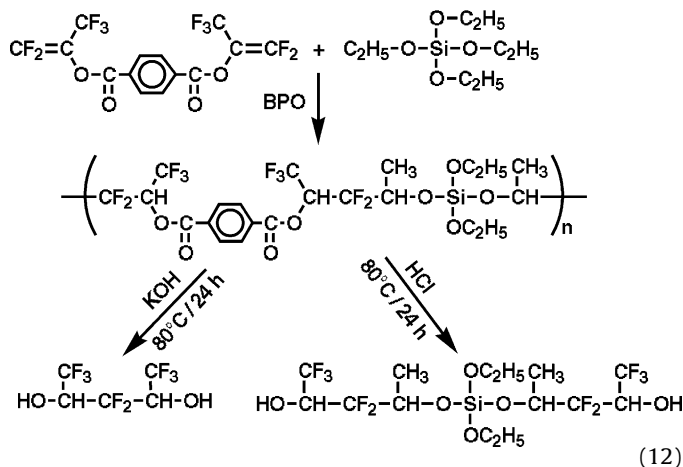
2.11. Conclusion

Radical addition reactions mentioned above make it possible to incorporate fluorinated vinyl compounds, whose homopolymerization reactivity is poor, into several organic compounds possessing carbon–hydrogen bonds by the aid of fluorine substituents although typical hydrocarbon analogues produce polymers under the radical condition. Di-addition products of DOX were yielded by the reaction of BPFP, BFP and PPVE. The fluorines of $CF_2=$ group may play an important role in the radical transfer reaction which takes place in the reaction intermediate, probably because the repulsion between two fluorine atoms might promote the cyclized structure of reaction intermediate to assist the radical transfer as shown in Scheme 1. The reaction of PPVE with DOX may be applicable to the preparation of polymers by the polyaddition of perfluorinated α,ω-divinyl compounds with DOX. It is proposed that the precise radical transfer may make it possible for novel organic syntheses to be practicable.

3. Anionic addition and polyaddition

The anionic polymerization reactivity of fluorinated vinyl monomers is generally higher than that of hydrocarbon analogues since initiators of relatively lower reactivity are preferable to afford polymers, as has been reviewed previously [1,19]. For example, the polymerization of 2-trifluoromethylacrylates yielded polymers by the initiators of relatively low reactivity such as alkali metal *tert*-butoxides and organoaluminum compounds although methyl methacrylate polymers are obtained by organolithium and organomagnesium as initiators. The addition reactivity of 2-trifluoromethylacrylates and related fluorinated vinyl monomers is hence higher toward anionic species than that of hydrocarbon analogues. To develop the high anionic addition reactivity of fluorinated vinyl monomers, Michael addition and the polyaddition by the double Michael reaction were investigated.

Pseude-first order rate constants with diethyl(ethyl cyanoace-tato)aluminum $[(C_2H_5)_2Al(NCCHCOOC_2H_5)]$ (Et$_2$AlECA) were determined to establish the reactivity order of several fluorinated acrylates and methacrylates. It was also investigated to establish the relationship between pseudo-first order rate constants of 18 fluorinated acrylates and methacrylates and spectroscopic data of the monomers. A quantitative elucidation of the reactivity order of fluorinated acrylates and methacrylates was proposed.

3.1. Anionic addition and polyaddition of 2-trifluoromethylacrylate

It is well-known that the Michael addition of active methylene compounds such as acetylacetone (acac), alkyl acetoacetate,

dialkyl malonate, alkyl cyanoacetate and malononitrile with vinyl compounds such as acrylonitrile, acrylates and vinyl ketones takes place easily under anionic conditions. The double Michael reactions of active methylene compounds have also been reported by quite a few research groups. However no polymer syntheses by double Michael addition reactions have been available. Acrylonitrile and methyl vinyl ketone show the high reactivity to the carbanion to yield double Michael addition products with active methylene compounds such as diethyl malonate and ethyl cyanoacetate $[NCCH_2COOC_2H_5]$ (ECA) which work as difunctional compounds under specific reaction conditions. The high reactivity of 2-trifluoromethylacrylates as an anion acceptor might be developed to the preparation of polymers by the double Michael reaction [20].

The results of the reaction of phenyl 2-trifluoromethylacrylate (PFA) with ECA catalyzed by CH_3CH_2ONa or NaOH are shown in Table 3 [20]. The suitable reaction condition to obtain the di-addition product of PFA with ECA is concluded to be those of Runs 5 and 9 to afford carbon–carbon bonds. These conditions may be applicable to the preparation of polymers by the anionic polyaddition by the double Michael addition reaction since ECA is found to perform as a difunctional compound with 2-trifluoromethylacrylate derivatives. The facile carbon–carbon bond formation is achieved by the double Michael addition of ECA with PFA under moderate reaction conditions.

The postulated reaction mechanism of the double Michael addition of PFA with ECA is depicted in Scheme 7 [20]. The mono-addition product is yielded by the addition reaction of the ECA anion (ECANa) to PFA followed by the ion transfer to afford the sodium salt of the ECA moiety in the reaction intermediate. The addition of PFA with the transition intermediate yields the di-addition compound followed by affording ECANa again.

Based on the results of the model reaction, the anionic polyaddition was examined. The results of polyaddition of 1,4-phenylene bis(2-trifluoromethylacrylate) $[CH_2=C(CF_3)COOC_6H_4OCOC(CF_3)=CH_2]$ (PBFA) with ECA by the double Michael addition reaction are shown in Table 4 [20]. The increase of ECA added into the reaction systems catalyzed by CH_3CH_2ONa in ethanol increases the yields and molecular weights of polymers obtained (Runs 1, 4, 6 and 10). The highest molecular weight is 1.2×10^4 (Run 5). The yield and molecular weight of the polymer are satisfactorily high with the large excess amount of ECA added into the reaction system (Run 9). The scarce increase in yields and molecular weights are observed by increasing the amount of CH_3CH_2ONa added (Runs 10 and 12). The gel formation takes place under the condition catalyzed by NaOH (Runs 15 and 16) which affords higher yields of the di-addition product shown in Run 9 in Table 3.

Table 3
Double Michael addition of PFA with ECA [20].

Run	1	2	3	4	5	6	7	8	9
ECA (mmol)	2.5	2.5	5.0	12.5	25.0	5.0	5.0	5.0	5.0
Solvent	EtOH	EtOH	EtOH	EtOH	EtOH	THF	THF	THF	THF
Base	EtONa	EtONa	EtONa	EtONa	EtONa	EtONa	EtONa	EtONa	NaOHaq
Base (mmol)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.25
Temperature (°C)	−20	60	60	60	60	60	60	60	r.t.
Time (day)	1	1	3	3	1	1	2	5	1
Reaction product (%)[a]									
Diadduct	0	41.7	56.6	64.8	71.1	50.0	56.9	57.1	84.6
Monoadduct	0	3.8	9.7	16.0	18.8	4.3	2.5	5.4	0
Ethoxide adduct	0	45.2	29.4	14.0	2.9	5.0	10.3	9.1	0
PFA	100	7.0	1.5	1.4	0	35.8	18.5	3.7	0
Others	0	2.3	2.8	3.8	7.2	4.9	11.8	24.7	15.4
Yield (%)[b]	–	12.1	37.0	33.8	49.6	20.6	49.6	38.6	–

PFA: 2.5 mmol, solvent: 5 mL.
[a] Measured by GC area ratio.
[b] Isolated yield of diaddition product.
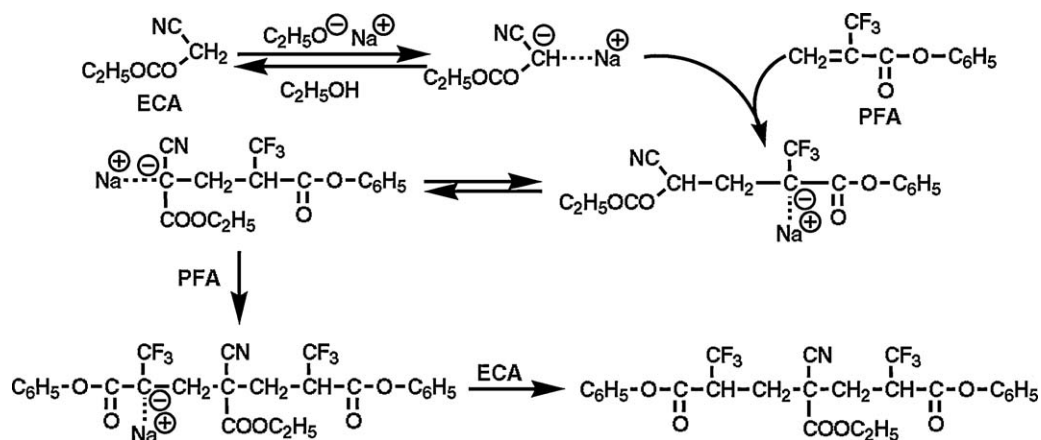
Scheme 7. Mechanism of the reaction of PFA with ECA [20].

The gel formation is also observed when reactions are carried out at room temperature (Runs 8 and 11).

The anionic polyaddition is concluded to take place by the double Michael addition as shown in Eq. (14) since the NMR spectrum of the polymer was similar to that of the di-addition product of the model reaction. Almost all polymer end groups were ECA moieties and a small amount of ethoxide-terminated polymer was detected by the NMR measurement.

trifluoromethylvinyl group at the chain end with CH_3CH_2ONa. The polyaddition reaction would be terminated when the addition reaction of the ethoxide anion to trifluoromethylvinyl group took place.

The monomer-addition experiment utilizing ECA moieties at the ends of polymer chains was carried out by the reaction of the polymer from PBFA with ECA by adding PBFA (2.5 mmol), ECA (25 mmol), CH_3CH_2ONa (0.25 mmol) and ethanol (5 mL) at 60 °C

$$(14)$$
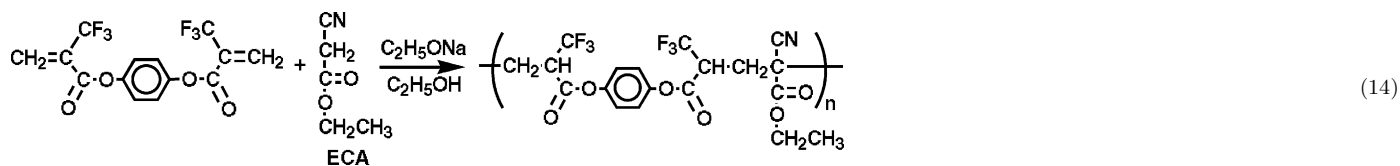
The postulated reaction mechanism is shown in Scheme 8 [20]. This is similar to that of Scheme 7 on the addition reaction of ECA anion to the PBFA moiety at the polymer chain end followed by sodium ion transfer to the ECA moiety at the chain end to yield sodium salt again. The addition of PBFA takes place followed by producing the ECA anion again. The polymer might be yielded by this cycle. Groups of polymer chain ends would then mainly be cyanoacetate moieties when a large excess amount of ECA was added in the reaction system. A small amount of the ethoxide-terminated polymer is also produced by the reaction of the

for 3 h. The polymer was isolated by sampling 1 mL of the reaction mixture followed by adding it to a large amount of methanol as a reprecipitation solvent to obtain polymer A. PBFA (1.25 mmol) was added to the reaction mixture, and kept at 60 °C for 1 more day followed by the reprecipitation to obtain polymer B. The THF (2 mL) solution of polymer B (0.5 g), CH_3CH_2ONa (0.1 mmol in ethanol) and PBFA (0.2 mmol) was kept at room temperature for 1 day and reprecipitated by methanol to obtain polymer C. Number-average molecular weight and molecular weight distribution ($\overline{M}_w/\overline{M}_n$) were: polymer A; 0.75×10^4 and 2.4, polymer B;

Table 4
Double Michael polyaddition of PBFA with ECA [20].

Run	ECA (mmol)	Solvent	Base (mmol)		Temperature (°C)	Time (day)	Yield (%)	$\overline{M}_n$ ($\times 10^4$)[a]	$\overline{M}_w/\overline{M}_n$[a]
1	2.5	EtOH	EtONa	0.25	60	1	50.4	0.44	1.7
2	2.5			0.25	60	1	39.4	0.64	1.7
3	5.0			0.25	60	1	84.7	0.61	4.4
4	5.0			0.25	60	1	52.7	0.84	2.7
5	5.0			0.5	60	1	21.0	1.2[b]	2.9[b]
6	12.5			0.25	60	1	52.7	1.0	2.4
7	12.5			0.5	60	1	59.7	1.1	8.3
8	12.5			0.5	rt	1	Gel	0.72[b]	3.2[b]
9	25.0			0.25	60	1	73.0	0.98	2.5
10	25.0			0.25	60	1	61.6	0.83	1.8
11	25.0			0.25	rt	1	Gel	1.1[b]	4.8[b]
12	25.0			0.5	60	1	67.8	0.89	2.1
13	25.0			0.5	60	1	35.8	0.46	2.1
14	25.0			0.5	60	2	31.9	0.56	1.7
15	5.0	THF	NaOHaq	0.25	rt	26 (min)	Gel	–	–
16	5.0			0.25	rt	1(h)	Gel	–	–

PBFA: 2.5 mmol, solvent: 5 mL.
[a] Determined by SEC (PSt Standards, eluent: THF).
[b] THF soluble part.
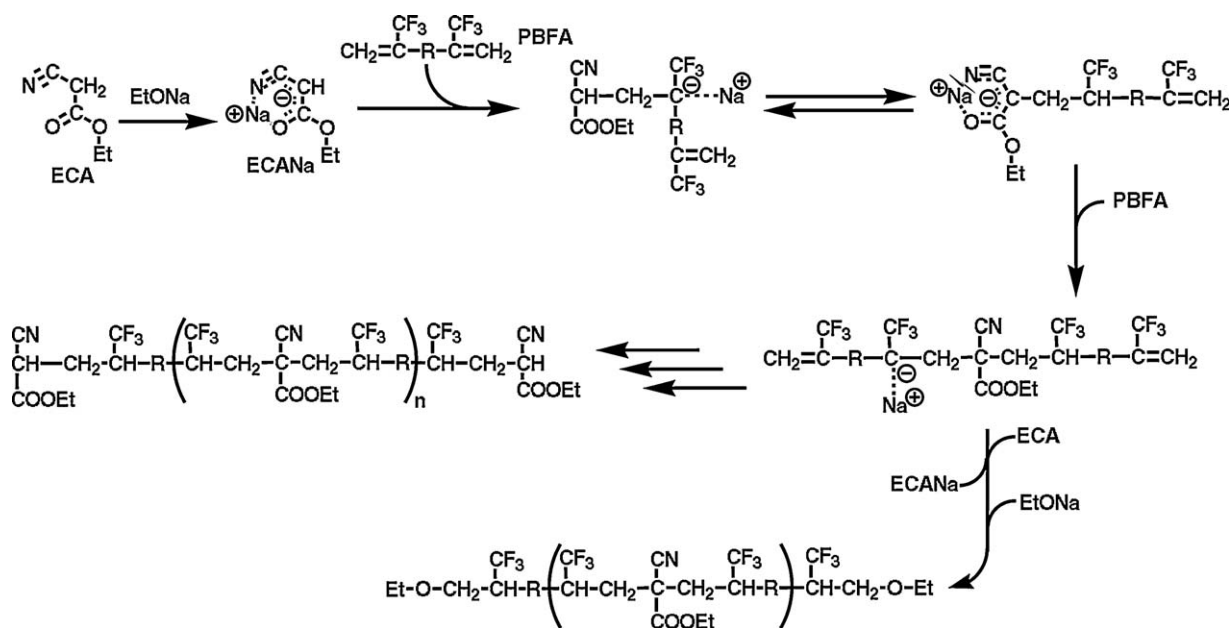
Scheme 8. Anionic polyaddition mechanism of PBFA with ECA; R = –COOC$_6$H$_4$OCO– [20].

0.91×10^4 and 1.8, and polymer C; 2.8×10^4 and 8.4, respectively. The drastic increases of the number-average molecular weight and broadening of the molecular weight distribution of polymer C are observed. This may be the evidence which shows that the end groups of a polymer are mainly cyanoacetate moieties.

The reaction conditions of the polyaddition of PBFA with acac by the double Michael addition reaction were also investigated. NaOH catalyzed Michael addition was found to be preferable. The results of NMR measurements of the polymer were similar to that of the di-addition product of PFA with acac. It might be concluded that the polymer contains PBFA and acac moieties. The highest molecular weight was 7.6×10^3 in THF and 1.4×10^3 in ethanol.

It is concluded that the double Michael addition reaction affords a facile method for the preparation of carbon–carbon bonds by the aid of trifluoromethyl substituent. The preparation of polymers by the anionic polyaddition may be a new field in the synthetic macromolecular chemistry. The high reactivity of fluorinated vinyl groups as an anion acceptor makes it possible to produce new types of polymers by the double Michael addition reaction of active methylene compounds. The polymer produced here may encourage to elaborate fluorinated functional polymers since it possesses several functional groups to be developed.

3.2. Initiation reaction of anionic polymerization

As has been demonstrated previously [1], the anionic polymerization of fluorinated acrylates and methacrylates shows the unique reactivity, which indicates that the electron density of vinyl groups would be reduced by the highest electronegativity of fluorine atoms, and the reactivity of vinyl monomers towards carbanions may be increased. The polymerization of 2-trifluoromethylacrylates produces polymers with anionic initiators of the relatively low reactivity such as alkali metal *tert*-butoxides, organozinc compounds, and organoaluminums. The monomers scarcely yield polymers by the initiation of typical anionic initiators such as organolithiums or organomagnesiums, probably because a carbonyl addition reaction took place simultaneously to terminate the polymerization.

The momentous report on the systematic investigation on the nucleophilic Michael addition reactivity onto α,β-unsaturated carbonyl compounds such as acrylates, methacrylates, and vinyl ketones has been reviewed by Prof. Emeritus T. Tsuruta [19].

To compare the reactivity of fluorinated acrylates and methacrylates under the anionic condition quantitatively, the pseudo first-order rate constants of the reactions of Et$_2$AlECA with several fluorinated acrylates and methacrylates were explored in the presence of excess amounts of fluorinated monomers [21]. The initiation reactivity of Et$_2$AlECA was found to be moderate compared to that of typical anionic initiators such as butyllithium and organomagnesiums. The Michael addition reaction would be supposed to exclusively take place in the reaction systems without the carbonyl addition and the hydrogen abstraction reactions which are often observed by the initiators of the relatively high reactivity such as alkyllithium or organomagnesium. Therefore, Et$_2$AlECA might be the most suitable candidate to establish the order of reactivity of fluorinated acrylates and methacrylates. The reaction was supposed to take place solely as depicted in Eq. (15).

$$(15)$$
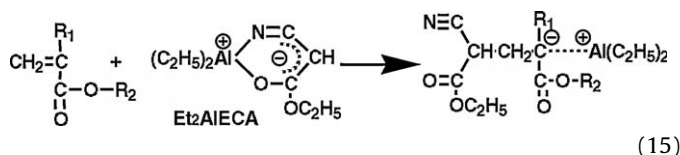
The results of pseudo first-order rate constants and spectroscopic characteristics such as ^{13}C NMR chemical shifts of β-carbons and carbonyl carbons, and IR absorptions of carbonyl groups are summarized in Table 5 [21].

The order of pseudo first-order rate constants of Et$_2$AlECA with 2-trifluoromethylacrylate derivatives is as follows: CH$_2$=C(CF$_3$)COOC$_2$H$_5$ > CH$_2$=C(CF$_3$) COOCH(CH$_3$)$_2$ > CH$_2$=C(CF$_3$)COOC (CH$_3$)$_3$ > CH$_2$=C(CF$_3$)COOCH$_2$C$_6$F$_5$ > CH$_2$=C(CF$_3$)COOCH(CF$_3$)$_2$ ≥ CH$_2$=C(CF$_3$)COOCH$_2$CF$_3$. The reactivity of CH$_2$=C(CF$_3$)COOC$_2$H$_5$ is extremely higher than that of CH$_2$=C(CH$_3$)COOCH$_3$, which demonstrates that the electron density of a vinyl group may be decreased by the electron-withdrawing inductive effect of the 2-trifluoromethyl group. The reactivity of CH$_2$=C(CF$_3$)COOC$_2$H$_5$ is higher than that of CH$_2$=C(CF$_3$)COOCH$_2$CF$_3$, which shows that one more trifluoromethyl substitution decreases the reactivity toward the carbanion although trifluoromethyl group in ester alkyl is linked four single bonds away from the vinyl group. Similar

Table 5
Pseudo-first order rate constants and spectroscopic data [21].

Run	Monomer	Temperature (°C)	$5 + \log k'$	e-Value[a]	β-Carbon (ppm)[b]	C=O (ppm)[b]	C=O (cm^{-1})[c]
1	$CH_2=C(CH_3)COOCH_3$	40	0.81	0.4	125.3	167.9	1732
2	$CH_2=C(CH_3)COOCH(CH_3)_2$	40	0.40	0.10	124.8	166.9	1718
3	$CH_2=C(CH_3)COOCH_2C_6H_5$	40	0.68	0.42	125.7	167.1	1716
4	$CH_2=C(CH_3)COOCH_2CF_3$	40	−0.05	0.98	127.7	165.6	1738
5	$CH_2=C(CH_3)COOCH_2C_2F_5$	40	0.00	–	127.8	165.5	1743
6	$CH_2=C(CH_3)COOCH_2C_6F_5$	40	1.56	0.48	126.5	166.5	1727
7	$CH_2=C(CH_3)COOCH(CF_3)_2$	0	–[d]	–	129.7	163.9	1758
8	$CH_2=C(CH_3)COOCH_2CH_2C_8F_{17}$	40	0.53	–	126.3	166.9	1728
9	$CH_2=C(CF_3)COOC_2H_5$	0	1.69	2.9	132.5	161.3	1740
10	$CH_2=C(CF_3)COOCH(CH_3)_2$	0	1.59	–	132.1	160.7	1736
11	$CH_2=C(CF_3)COOC(CH_3)_3$	0	1.39	–	131.6	160.4	1736
12	$CH_2=C(CF_3)COOCH_2CF_3$	0	0.62	–	134.7	159.6	1760
13		40	1.87	–	134.7	159.6	1760
14	$CH_2=C(CF_3)COOCH_2C_6F_5$	0	1.35	–	133.9	160.6	1747
15	$CH_2=C(CF_3)COOCH(CF_3)_2$	0	1.26	–	136.4	158.1	1776
16		40	1.71	–	136.4	158.1	1776
17	$CH_2=CHCOOCH_3$	0	0.84	0.6	130.6	166.6	1731
18[e]		40	1.89	0.6	130.6	166.6	1731
19	$CH_2=CHCOOCH_2C_6H_5$	0	0.68	1.13	131.0	165.9	1726
20	$CH_2=CHCOOCH_2CF_3$	0	−0.05	1.13	133.0	164.4	1762
21		40	1.47	1.13	133.0	164.4	1762
22	$CH_2=CHCOOCH_2C_2F_5$	40	1.31	–	133.2	164.3	1751
23	$CH_2=CHCOOCH_2C_6F_5$	0	1.48	–	131.9	165.2	1736
24	$CH_2=CHCOOCH(CF_3)_2$	40	1.14	1.36	135.3	162.6	1763
25	$CH_2=CHCOOCH_2CH_2C_8F_{17}$	40	1.74	–	131.5	165.6	1736
26	$CH_2=CFCOOC(CF_3)_3$	40	–[d]	–	101.4	159.4	1739
27	$CH_2=CFCOOCH_2C_2F_5$	40	–[d]	–	104.8	158.7	1767

[a] Ref. [1].
[b] Determined by ^{13}C NMR in CDCl$_3$.
[c] Determined by IR.
[d] Unable to be measured because of too fast polymerization.
[e] In toluene.

phenomenon is indicated in the case of $CH_2=C(CF_3)COOCH(CH_3)_2$ and $CH_2=C(CF_3)COOCH(CF_3)_2$, which shows the lower reactivity. The reactivity of $CH_2=C(CF_3)COOCH(CH_3)_2$ is higher than that of $CH_2=C(CF_3)COOC(CH_3)_3$, probably because of the bulkiness of substituents.

The order of pseudo first-order rate constants of Et$_2$AlECA with fluoroalkyl methacrylates is as follows: $CH_2=C(CH_3)COOCH_2C_6F_5 > CH_2=C(CH_3)COOCH_3 > CH_2=C(CH_3)COOCH_2C_6H_5 \geq CH_2=C(CH_3)COOCH_2CH_2C_8F_{17} > CH_2=C(CH_3)COOCH(CH_3)_2 > CH_2=C(CH_3)COOCH_2C_2F_5 \geq CH_2=C(CH_3)COOCH_2CF_3$. It is well-known that the anionic polymerization of $CH_2=C(CH_3)COOCH_3$ hardly takes place by the initiation of organoaluminums. The incorporation of trifluoromethyl substituent as an ester group surely increases the polymerization reactivity as far as the yields of polymers were concerned since the polymer yield of $CH_2=C(CH_3)COOCH_2CF_3$ was much higher than that of $CH_2=C(CH_3)COOCH_3$ initiated with organoaluminums. On the contrary, the rate constants of fluoroalkyl methacrylates except $CH_2=C(CH_3)COOCH_2C_6F_5$ are smaller than that of $CH_2=C(CH_3)COOCH_3$ although the rate constants of fluorinated methacrylates are almost the same order of magnitude to that of $CH_2=C(CH_3)COOCH_3$ [1]. The reactivity of $CH_2=C(CH_3)COOCH_2C_6F_5$ is considerably higher than that of $CH_2=C(CH_3)COOCH_2C_6H_5$ although Q,e-values of $CH_2=C(CH_3)COOCH_2C_6F_5$ are 0.61 and 0.48, respectively, which are similar to those of $CH_2=C(CH_3)COOCH_2C_6H_5$. Pentafluorophenyl group linked four single bonds away from the vinyl group exhibits a large effect on the reactivity of the vinyl group. The rate constants of $CH_2=C(CH_3)COOCH_2C_2F_5$ and $CH_2=C(CH_3)COOCH_2CH_2C_8F_{17}$ are similar to that of $CH_2=C(CH_3)COOCH_3$. The reactivity of $CH_2=C(CH_3)COOCH_2CH_2C_8F_{17}$ might be influenced by one more methylene spacer group in ester alkyl group. The incorporation of trifluoromethyl substitution is scarcely effective since the rate constant of $CH_2=C(CH_3)COOCH_2CF_3$ is not much larger than that of $CH_2=C(CH_3)COOCH_3$. It is concluded that the incorporation of the

higher fluorine substitution decreases the reactivity toward the carbanion in the series of fluoroalkyl methacrylates except pentafluorophenylmethyl group.

The 2-trifluoromethyl substitution shows much higher effect on the reaction with the anion since the rate constant of $CH_2=C(CF_3)COOCH_2CF_3$ is drastically larger than that of $CH_2=C(CH_3)COOCH_2CF_3$. No polymerization conditions of 1-trifluoromethylstyrene [$CH_2=C(CF_3)C_6H_5$] have been reported although the hydrocarbon analogue produces easily polymers under radical and anionic conditions, which is another example that the trifluoromethyl group linked to a vinyl group shows extremely large effect on the reactivity of the vinyl compound.

The order of pseudo first-order rate constants of Et$_2$AlECA with fluoroalkyl acrylates is as follows: $CH_2=CHCOOCH_2C_6F_5 > CH_2=CHCOOCH_3 > CH_2=CHCOOCH_2CH_2C_8F_{17} > CH_2=CHCOOCH_2C_6H_5 > CH_2=CHCOOCH_2CF_3 > CH_2=CHCOOCH_2C_2F_5 > CH_2=CHCOOCH(CF_3)_2$. The anionic polymerization of $CH_2=CHCOOCH_3$ easily takes place by the initiation with organoaluminums on the contrary to the polymerization of $CH_2=C(CH_3)COOCH_3$. The similar reactivity order to that of fluoroalkyl methacrylates is demonstrated, because the incorporation of more fluorinated groups decreases the reactivity toward the carbanion except pentafluorophenylmethyl group. The effect of the bulkiness may appear in the case of $CH_2=CHCOOCH_2C_2F_5$ and $CH_2=CHCOOCH(CF_3)_2$. Rate constants of $CH_2=CFCOOC(CH_3)_3$ and $CH_2=CFCOOCH_2C_2F_5$ were unable to be measured because of too fast polymerization. The polymer yields and number-average molecular weights produced by the initiation of Et$_2$AlECA at 40 °C for 7 days in toluene were 20.3%, 1.7×10^4 for $CH_2=CFCOOC(CH_3)_3$ and 12.1%, 3.4×10^4 for $CH_2=CFCOOCH_2C_2F_5$, respectively.

The reactivity of the fluoroalkyl acrylate is intermediate between the 2-trifluoromethylacrylate and the methacrylate since the order of rate constants is $CH_2=C(CF_3)COOCH_2CF_3 > CH_2=CHCOOCH_2CF_3 > CH_2=C(CH_3)COOCH_2CF_3$. The effect of the penta-
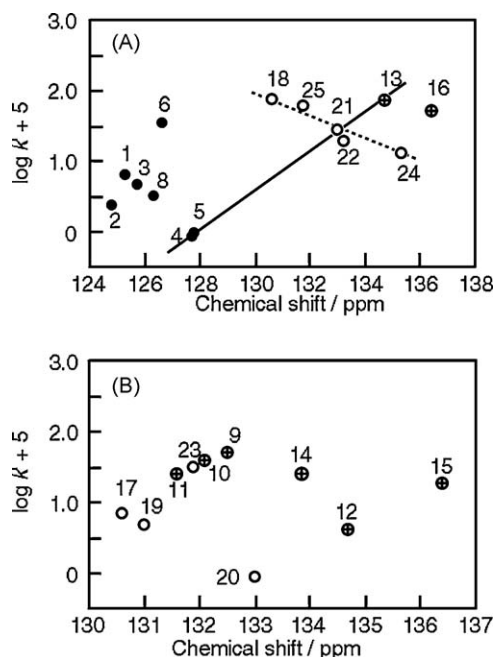
Fig. 1. Log k' at 40 °C (A) and at 0 °C (B) vs. ^{13}C NMR chemical shifts of β-carbons of fluorinated acrylates and methacrylates (refer to Table 5) (⊕) 2-trifluoromethylacrylate; (●) methacrylate; (○) acrylate [21].

Fig. 2. Log k' at 40 °C (A) and at 0 °C (B) vs. ^{13}C NMR chemical shifts of carbonyl carbons of fluorinated acrylates and methacrylates (refer to Table 5) (⊕) 2-trifluoromethylacrylate; (●) methacrylate; (○) acrylate [21].

fluorophenylmethyl group as an ester group seems to be different from that of other fluoroalkyl groups since the reactivity order is $CH_2=CHCOOCH_2C_6F_5 > CH_2=C(CF_3)COOCH_2C_6F_5 > CH_2=C(CH_3)COOCH_2C_6F_5$. The effect of the pentafluorophenyl group in pentafluorostyrene [$CH_2=CH–C_6F_5$] is scarcely detected since no polymer was obtained by organoaluminums.

The relationship between log k' and ^{13}C NMR chemical shifts of β-carbons of fluorinated acrylates and methacrylates is depicted in Fig. 1 [21]. The linear relationship between log k' and chemical shifts of fluorinated acrylates (18, 21, 22, 24 and 25) is shown in Fig. 1(A) although the poor dependency is indicated in the case of 2-trifluoromethylacrylates and methacrylates. The linear relationship is shown in the case of 2,2,2-trifluoroethyl esters such as $CH_2=C(CH_3)COOCH_2CF_3$ (4), $CH_2=CHCOOCH_2CF_3$ (21), and $CH_2=C(CF_3)COOCH_2CF_3$ (13). Pseudo first-order rate constants of $CH_2=CFCOOC(CH_3)_3$ and $CH_2=CFCOOCH_2C_2F_5$ might be drastically different from those of other fluoroalkyl acrylates since chemical shifts of β-carbons are 101.4 and 104.8 ppm, respectively, which are considerably smaller than those of other fluoroalkyl acrylates.

The relationship between log k' and ^{13}C NMR chemical shifts of carbonyl carbons of fluorinated acrylates and methacrylates is summarized in Fig. 2 [21]. A certain relationship between log k' and chemical shifts of acrylates (18, 21, 22, 24 and 25) and methacrylates (1, 2, 3, 4, 5, and 8) is shown in Fig. 2(A), and some dependency is shown in Fig. 2(B) in the case of 2-trifluoromethylacrylates (9, 10, 11, 12, 14, and 15) and acrylates (17, 19, 20 and 23).

The relationship between log k' and wave numbers of carbonyl groups of fluorinated acrylates and methacrylates measured by IR is shown in Fig. 3 [21]. No obvious relationship between log k' and the wave numbers seems to be demonstrated.

As far as the pseudo first-order rate constants are concerned, a delicate dependency on the spectroscopic data has totally evidenced and it will not be enough to help a quantitative anticipation of the reactivity of these fluorinated monomers. A more detailed concept covered all the monomer reactivity order should be needed. This might strongly suggest that the quantitative investigation on the propagation reaction is important to
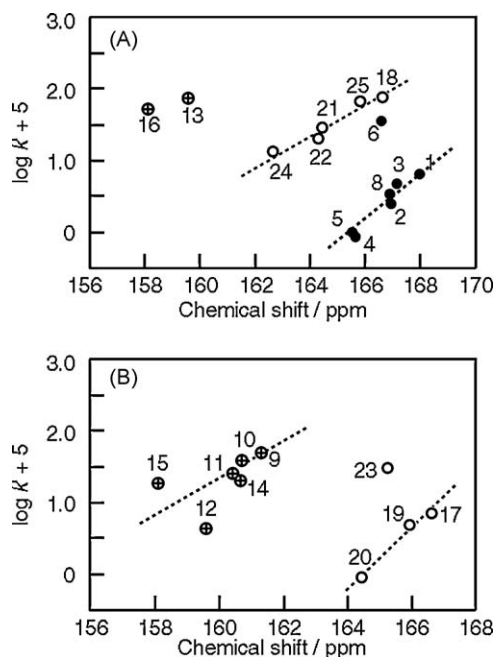
clarify the total polymerization reactivity although the polymerization of these monomers is complicated when initiated by organolithium, since several elementary reactions such as conjugate addition, carbonyl addition, chain transfer, and termination reactions would take place. The propagation reactivity might be influenced by the same effect as that of the initiation reaction by the incorporation of fluorine and fluoroalkyl substituents because the electron density of the propagating anion would also be decreased.

It might be desirable to calculate the reactivity order of fluorinated acrylates and methacrylates by computer chemistry to
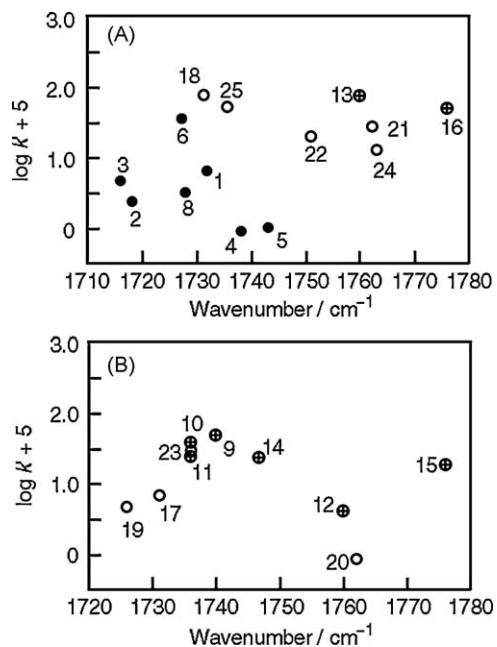

Fig. 3. Log k' at 40 °C (A) and at 0 °C (B) vs. infrared absorption of carbonyl groups of fluorinated acrylates and methacrylates (refer to Table 5) (⊕) 2-trifluoromethylacrylate; (●) methacrylate; (○) acrylate [21].

present which components would control the reactivity based on the data shown in Table 5.

3.3. Conclusion

The high reactivity of 2-trifluoromethylacrylates as a good acceptor of anionic species is demonstrated since the pseudo-first order rate constants of the reactions of 2-trifluoromethylacrylates with the cyanoacetato anion are the highest compared to those of acrylates and methacrylates. This leads to the anionic polyaddition to afford new types of fluorinated polymers possessing functional groups besides fluorines. It is proposed that the anionic reactivity order of fluorinated acrylates and methacrylates derived from pseudo-first order rate constants may contribute to the development in the field of computer chemistry to find out which effect of fluorine-substitution would mainly control the reactivity.

4. Cationic polymerization in the presence of perfluoroisopropenyl compound

The polymerization of fluorine-containing vinyl monomers has mainly been focused on radical polymerization. It can probably be concluded that the investigation of the radical homopolymerization reactivities of fluorinated vinyl monomers possessing fundamental structures has almost been completed, and many fluorinated vinyl monomers have been found to yield no corresponding homopolymers under moderate radical polymerization conditions except tetrafluoroethylene and chlorotrifluoroethylene. The polymerization reactivity of BPFP is in almost the same situation. To incorporate perfluorovinyl and perfluoroisopropenyl segments into polymer main chains, copolymerizations with vinyl ethers under radical conditions are well-known methods which generally yield alternating copolymers. On the course of radical copolymerizations of BPFP with vinyl ether and N-vinylcarbazole (NVC) to produce alternating copolymers, unexpected results have been obtained [22].

The radical copolymerization of butyl vinyl ether (BVE) with BPFP was carried out initiated with BPO in order to obtain alternating copolymers. BVE is a compound which is well-known to yield a homopolymer under cationic condition and no polymerization takes place with a radical initiation. No polymer was obtained when no solvent was added. Polymers were produced in benzene as a polymerization solvent in low yields at 80 °C. ^{1}H NMR of the product showed no absorptions of phenyl protons. The spectrum was therefore in accord with that of the homopolymer of BVE produced under a traditional cationic condition. The homopolymerization of BVE should then take place in the reaction system. The polymerization at a low temperature was investigated since it is well-known the BVE homopolymerization usually takes place through a cationic mechanism in lower temperature. High yields of poly(BVE) were obtained at 0 and −78 °C. Then, the polymerization in the absence of BPO was examined. Polymers of BVE were obtained in high yields with 1.6×10^5 as the highest molecular weight. Instead, a trace amount of the polymer was yielded without the addition of BPFP. This firmly suggested that BPFP performed as an initiator of the cationic polymerization!

Another example was investigated by the polymerization of NVC which is a compound well-known for producing a homopolymer only under cationic conditions. The yield of the obtained polymer increased with an increase in the amount of BPFP added to the reaction system at 0 and −78 °C, and poly(NVC) with 5.2×10^4 as the highest molecular weight was obtained. The polymer was produced with a small amount of BPFP added (even at 1 mol%).

It has been confirmed that the some cationic species may be yielded by the addition of BPFP since no evidence which shows the initiation by HF is available. This may be another gift of serendipity.

5. Conclusions

All the reactions introduced in this article take place by the contribution of fluorine-substituents and no similar reactions have ever been reported by the research achievement in the field of hydrocarbon analogues. The reactions provide facile methods for the carbon–carbon bond formation which is one of the most important reactions in the field of organic chemistry to form a framework of a compound. The reactions are totally ascribable to the fluorinated substituent effect. Many of the reactions described here can be carried out by very simple reaction systems to handle. The introduction of fluoroalkyl substituents into organic compounds possessing carbon–hydrogen bonds is easily achieved. Organic syntheses through polymerization are also proposed by employing the precise radical shift mechanism. Quite a few fluorinated vinyl compounds which hardly afford the corresponding homopolymers under conventional reaction conditions can be utilized as starting materials for the preparation of fluoroalkyl compounds and novel fluorinated polymers by the new findings. Another important approach is to carry out a study in a neighboring research field because a gift from serendipity may be presented. Fluorine is "Small atom with a big ego" [23]. It should be stressed again that it is important to knock on the door of the house of each fluorinated vinyl monomer to ask how the resident wants to act, and to accumulate the statements [1].

As you sow, so will you reap.

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