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NOTES

Anionic Polymerization of 2,3,4,5,6-Pentafluorostyrene

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A series of ionic polymerization studies of several fluorine-containing vinyl monomers have previously been reported.[1–7] The high electron-withdrawing effect of fluoroalkyl substituents reduces electron density of the vinyl groups so that reactivity towards carbanions is increased. It has been pointed out that the e values of fluoroalkyl acrylates and methacrylates are so large that these monomers can easily undergo anionic polymerization with initiators of relatively low nucleophilicity. The same effect has been observed on the anionic polymerization of *o*- and *p*-trifluoromethylstyrenes.[8]

However, only a few reports on the anionic polymerization of fluorinated styrenes are available.[9] The reactivity of fluorinated styrenes such as 2,3,4,5,6-pentafluorostyrene (PFS) might be strongly influenced by the pentafluorophenyl moiety. Pryor and Huang[10] have shown the Q and e values of PFS to be 0.69 and 0.74, respectively, by radical copolymerization of PFS with styrene. PFS has such a large positive e value that the monomer is expected to be easily polymerized with anionic initiators.

The present paper deals with some examinations of anionic polymerization reactivity of PFS by various methods such as anionic polymerization initiated with several compounds, anionic copolymerization with styrene, and the calculation of charge distribution of PFS and propagating carbanionic end group by MNDO method.

EXPERIMENTAL

Most of the experiments related to polymerization reactions were carried out under purified nitrogen atmosphere to exclude oxygen and atmospheric moisture.

Reagents

Commercial 2,3,4,5,6-pentafluorostyrene (PFS) was purified by refluxing over CaH_2, followed by distillation under reduced pressure (bp 62°C/50 mmHg). Styrene was purified by the usual method. Toluene and tetrahydrofuran (THF) were refluxed over CaH_2 and then distilled under nitrogen. 1,2-Dimethoxy-

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ethane (DME) was purified by the same method and further purification was carried out by refluxing with $Al(C_2H_5)_3$ and distillation under nitrogen. Commercial n-C_4H_9Li and C_2H_5MgBr were used as initiators after determination of the concentrations of the active species by alkalimetry. t-C_4H_9OLi was purified by sublimation *in vacuo*. $LiAlC_4H_9(C_2H_5)_3$ and $(iso\text{-}C_3H_7)_2NLi$ were synthesized by reactions of $Al(C_2H_5)_3$ and $(iso\text{-}C_3H_7)_2NH$ with n-C_4H_9Li, respectively, under nitrogen. $(C_2H_5)_2$Alacac was synthesized from equimolar reaction of $Al(C_2H_5)_3$ and acetylacetone. Commercial $Al(C_2H_5)_3$, $Zn(C_2H_5)_2$, and $(iso\text{-}C_3H_7)NH$ were distilled under reduced pressure.

Procedures

A glass ampoule was charged with monomer (21.7 mmol), initiator (0.43 mmol) and solvent using a syringe under nitrogen (total volume: 20 ml). The ampoule was sealed and kept at a constant temperature and the reaction mixture was magnetically stirred. The polymer was isolated by reprecipitation with methanol and dried to a constant weight.

Composition of styrene–PFS copolymer was estimated from elemental analysis. Gel permeation chromatogram (GPC) was measured with a Hitachi L-6000 chromatograph equipped with a Gelpack R-400 M column using THF as an eluent. Charge distribution of monomer was calculated by the MNDO method.[11]

RESULTS AND DISCUSSION

The results of the polymerization of PFS with several anionic initiators are summarized in Table I. Based on the relationship between the reactivity of the vinyl monomers and that of anionic initiators proposed by Tsuruta,[12] monomers with high e values should produce polymers with anionic initiators of relatively low nucleophilicity. As shown in Table I, PFS can be polymerized with even pyridine which belongs to the group of the lowest nucleophilicity[12] though the polymer yield is low. Other initiators such as $LiAlC_4H_9(C_2H_5)_3$, $(C_2H_5)_2$Alacac, and $Zn(C_2H_5)_2$ can also produce polymers. PFS is found to show high reactivity towards anionic initiators. The highest yield is obtained with n-C_4H_9Li, and THF is preferable with regard to polymerization solvents. The products obtaineld here showed similar GPC curves. The molecular weight distribution was unimodal.

The anionic polymerization of PFS initiated with n-C_4H_9Li was investigated with variation of temperature and polymerization time. The yields of poly(PFS) increased with reaction temperature. At 60°C, it increased up to 43.5%. Higher temperature seems to be preferable for

Table I. Conditions and results of the polymerization of PFS at room temperature (*ca.* 25°C)

Initiator	Solvent	Time day	Yield %
n-C_4H_9Li	THF	7	16.6
	Toluene	7	1.8
	DME	7	7.7
C_2H_5MgBr	THF	7	4.8
$LiAlC_4H_9(C_2H_5)_3$	THF	7	3.6
t-C_4H_9OLi	THF	7	2.9
$(iso\text{-}C_3H_7)_2NLi$	THF	7	0
$(C_2H_5)_2$Alacac	THF	7	2.5
$(C_2H_5)_2Zn$	THF	16	6.6
	Toluene	16	0
Pyridine	THF	7	2.0

Table II. Polymerization of PFS with n-C_4H_9Li as a function of time at room temperature.[a]

Temp °C	Time day	Yield %	$M_n \times 10^{-4}$
Room temp.[b]	1	2.9	1.0
	7	16.6	5.2
	17	25.0	5.7
60	1	11.0	0.9
	7	43.5	3.7
	17	42.0	—

[a] In THF.

[b] *ca.* 25°C.

the polymerization of PFS.

Table II shows the relationship between reaction time and yields of poly(PFS) at room temperature (*ca.* 25°C) and 60°C. The yields increase continuously for 7 days. Molecular weights also increase with reaction time.

The copolymerization of PFS with styrene initiated by n-C_4H_9Li showed a similar copolymerization curve as that initiated by AIBN.[10] The monomer reactivity ratios r_1 (St) and r_2 (PFS) calculated by the Finemann–Ross method are 0.33 and 0.43, respectively. In the case of radical copolymerization, they are 0.43 and 0.22, respectively. The product r_1r_2 is less than unity which indicates a cross-propagating tendency of copolymerization.

As shown in Table I, initiators examined here are found to yield some polymeric products. In contrast styrene is polymerized only with the initiators of the highest reactivity such as n-C_4H_9Li,[12] and the polymerization reaction is completed within a few hours once the initiation reaction takes place.[13] To determine the reason for the difference between the reactivity of PFS and styrene, the calculations of the atomic charge of PFS and styrene were carried out by the MNDO method. The results are shown in Figure 1. The atomic charges of the β-carbons of styrene and PFS are -0.057 and -0.002, respectively. PFS can, therefore, react more readily with the carbanions of lower nucleophilicity because of the lower charge density of the β-carbon.

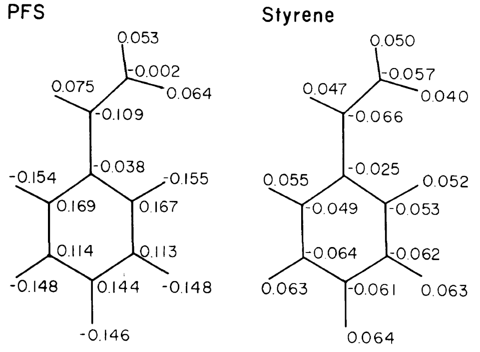

Figure 1. Atomic charge distribution of PFS and styrene calculated by means of MNDO method.

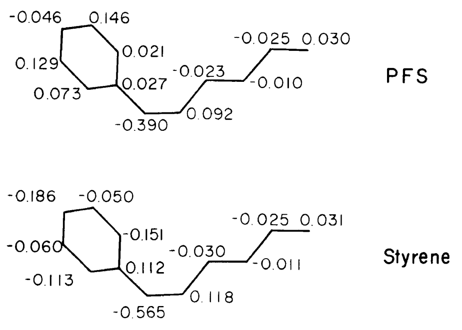

Figure 2. Atomic charge distribution of skeletal carbon atoms of PFS and styrene added to n-butyl anion.

The atomic charge calculation of the active species in anionic polymerization was also tried by the same method. The active species were regarded as 1-perfluorophenyl–n-hexyl and 1-phenyl–n-hexyl anions which are the adducts of the monomers and n-butyl anion. The results are shown in Figure 2. Atomic charges of the carbanions of the adducts of PFS and styrene are -0.390 and -0.565, respectively. The atomic charge of the carbanion on PFS-adduct is found to be more dispersed due to the electron-withdrawing effect of the fluorine atoms. The lower polymerization reactivity of PFS might, therefore, be controlled by the lower electron-density of propagating PFS anion end group.

In conclusion, the anionic polymerization reactivity of PFS is found to be higher than that of styrene since the polymerization of PFS takes place even with initiators of lower reactivity such as ate complexes, organoaluminum, organozinc and pyridine though apparent yields of polymers are relatively low. The anionic copolymerization of PFS with styrene seems to be largely controlled by the reactivities of both monomers and polymer anions as the cross-propagations are tend to take place. The reactivities of these monomers derived from polymer yields are supported by the atomic charge calculations of these monomers and the model compounds of the propagating polymer anion end groups.

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