Anionic living polymerization of 4-vinyl(*N,N*-diisopropylbenzamide)

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Anionic polymerization of 4-vinyl(*N,N*-diisopropylbenzamide) (**1**) was effected with cumyl potassium, poly(α-methylstyryl)lithium, and -potassium in tetrahydrofuran at −78°C. Compound **1** was readily polymerized under these conditions to form a 'living polymer'. Using this method, polymers of **1** with very narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n = 1.04$–$1.06$) were obtained in a quantitative conversion. The diblock copolymer, poly[α-methylstyrylene-*b*-4-vinyl(*N,N*-diisopropylbenzamide)], was also prepared.

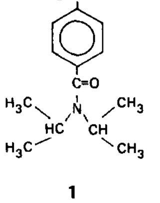
(Keywords: poly[4-vinyl(*N,N*-diisopropylbenzamide)]; living polymer; anionic polymerization; block copolymer)

INTRODUCTION

Anionic living polymerization provides a useful method for synthesizing polymers of predictable molecular weight and narrow molecular weight distribution and tailored block copolymers of uniform composition. It is generally agreed that the range of vinyl monomers capable of producing persistent living polymers is limited to nonpolar hydrocarbon monomers such as styrene, 1,3-butadiene and isoprene.

However, recently it has been reported that anionic polymerizations of styrene derivatives containing a metal or a functional group, e.g. 4-chlorostyrene[1], 4-bromostyrene[2], 4-dimethylaminostyrene[3,4], 4-trimethylsilylstyrene[5,6], 4-trimethylsilyl-α-methylstyrene[7], 4-tributyl- and 4-triphenyl-germylstyrenes[8], and 4-triphenyltin styrene[9], proceed without chain transfer and termination reactions and that block copolymers, having their respective polymer units, can be prepared. Recently, we have successfully carried out the anionic living polymerizations of 4-(t-butyldimethylsilyloxy)styrene and 4-*N,N*-bis(trimethylsilyl)aminostyrene. Consequently, poly(4-hydroxystyrene) and poly(4-aminostyrene) of a predicted molecular weight and a narrow molecular weight distribution were obtained after the complete deprotection of the silyl groups from the resulting polymers[10,11]. These findings outline a useful method by which functional-group containing polymers of a defined structure and narrow molecular weight distribution can be obtained.

We wish to report here the anionic polymerization of 4-vinyl(*N,N*-diisopropylbenzamide) (**1**) and present details concerning whether or not the anionic living polymerization of such a tertiary amide-containing monomer occurs.



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EXPERIMENTAL

Materials

4-Vinylbenzoic acid was kindly supplied by Hokko Chemical Industry Co. Ltd and was used without further purification. Commercial α-methylstyrene was purified by distillation over calcium hydride. Tetrahydrofuran (THF) was used as a solvent in all the polymerization experiments and was distilled from sodium wire and then from sodium naphthalide solution. Naphthalene was purified by sublimation. Cumyl potassium was prepared by reaction of cumyl methyl ether with potassium–sodium alloy in THF at room temperature for 10 h. The reaction mixture was filtered and the bright red coloured filtrate was colorimetrically titrated with standardized n-octanol to a colourless endpoint. Poly(α-methylstyryl) lithium and -potassium were prepared just prior to polymerization from n-butyllithium and potassium naphthalide, respectively, and a 2–4 molar quantity of α-methylstyrene at 30°C for 1 min and then at −78°C for 5 min. Standardization was performed similarly by titration. All the operations were carried out in reactors with breakseals under high vacuum ($\sim 10^{-6}$ mbar).

4-Vinylbenzoyl chloride

To a mixture of 4-vinylbenzoic acid (9.0 g, 61 mmol) and 4-t-butylpyrocathechol (10 mg), a portion (18 ml) of thionyl chloride was added dropwise under cooling. The reaction mixture was kept below 10°C for 5 h, and then gradually warmed to 40°C for 1 h. After removal of unreacted thionyl chloride, distillation gave 6.6 g (65%, b.p. 90°C–93°C/1 mbar) of pure 4-vinylbenzoyl chloride as a colourless liquid (literature[12] 69.5°C–70°C/0.1 mmHg). ^{1}H n.m.r. (CCl_4): 5.44, 5.88 (dd, 2H, $J = 10, 17$ Hz, $CH_2{=}CH{-}$); 6.78 (dd, 1H, $CH{=}CH_2$); 7.47, 8.08 (dd, 4H, $J = 10$ Hz, C_6H_4, a, b).

4-Vinyl(N,N*-diisopropylbenzamide*) (**1**)

4-Vinylbenzoyl chloride (6.55 g, 39.3 mmol) was dissolved in dry ether (30 ml) and the solution was cooled to 0°C–5°C. Diisopropylamine (11.1 ml, 78.6 mmol) in dry ether (150 ml) was then added dropwise at such a rate

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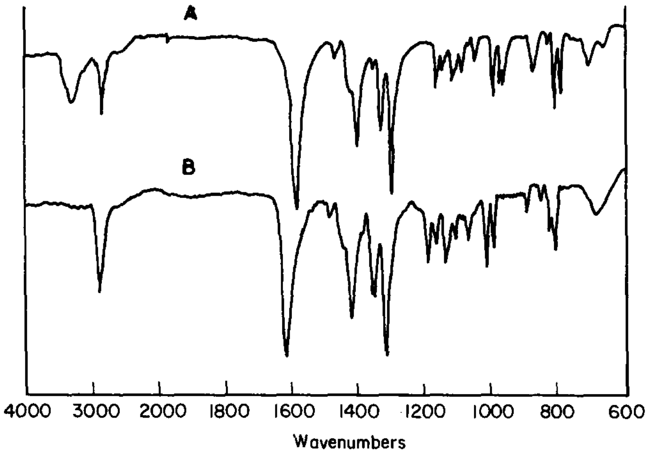

Figure 1 Infra-red spectra of (A) 4-vinyl(*N,N*-diisopropylbenzamide); and (B) of poly[4-vinyl(*N,N*-diisopropylbenzamide)

that the temperature did not exceed 5°C. The resulting mixture was stirred at 0°C–5°C for 2 h and then overnight at 20°C. The precipitated salt was filtered off and the filtrate was washed with $NaHCO_3$ saturated solution and water, and then dried with anhydrous Na_2SO_4. After evaporation of the ether, the residue was recrystallized from petroleum ether (30°C–60°C) and a small amount of benzene to yield pure white crystals of **1** (6.8 g; 75%; m.p. 82°C–83°C). ^{1}H n.m.r. (CCl_4): $\delta = 1.42$ (d, 12H, $J = 6$ Hz, $-(C\underline{H}_3)_2$), 3.73 (hep, 2H, $J = 6$ Hz, $N-C\underline{H}$), 5.32 ~ 5.80 (2d, 2H, $J = 10, 18$ Hz, $C\underline{H}_2=CH-$), 6.80 (2d, 1H, $-C\underline{H}=CH_2$), 7.30 ~ 7.50 (2d, 4H, $J = 9$ Hz, $C_6\underline{H}_4$, a, b). It was dried over P_2O_5 for 48 h in the reactor with a breakseal under vacuum (~10^{-6} mbar) and was used for anionic polymerization.

Polymerizations

Anionic polymerizations were carried out under high vacuum (10^{-6} mbar) in sealed glass reactors with breakseals by a method similar to that reported previously[13]. The reaction mixture was shaken and allowed to stand at −78°C for 0.5 h. After quenching with methanol, the polymers were precipitated into an excess of water, filtered off, redissolved in THF, and precipitated into water twice and finally into *n*-hexane. The purified polymers were freeze-dried from benzene for 12 h and then at 50°C for an additional 12 h.

Measurements

^{1}H n.m.r. spectra were recorded using a JEOL JNM-PMX60 spectrometer. Infra-red (i.r.) spectra were recorded on a JASCO IR-G spectrometer. Gel permeation chromatograms (g.p.c.) were obtained on a Toyosoda HCL-802 with u.v. or refractive index detection, THF being the elution solvent. Molecular weight measurements were made using a Corona 117 vapour pressure osmometer (v.p.o.) in benzene. Glass transition temperature was evaluated by d.s.c. on a Perkin–Elmer ESC-2 at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

Anionic polymerization of 1

To the best of our knowledge, there appeared to be no examples of anionic polymerization of substituted styrenes with tertiary amido groups, probably because one might have considered that the carbonyl carbon of amido group readily reacted with anionic initiators and propagating carbanions. In fact, *N,N*-dimethylbenzamide is susceptible to nucleophilic attack by butyl lithium. giving a species which is converted to valerophenone by hydrolysis[14]. However, it has been shown by Beak and Brown[15] that such a nucleophilic addition can be suppressed by employing sterically hindered lithium reagents and bulkier *N,N*-diethyl- or diisopropylbenzamide; under these conditions, the ortho lithiation of a phenyl ring occurs instead.

On the basis of these results, anionic polymerization of **1** was attempted in the hope that the initiator would attack not the amido group but the vinyl group of **1** to initiate polymerization. The polymerization of **1** was carried out with cumyl potassium as an initiator. A characteristic bright red colour was observed in the reaction mixture and apparently remained unchanged at −78°C for 1 h. Termination was accomplished by adding a few drops of methanol and the red colour disappeared immediately. The polymer produced was then precipitated by pouring the mixture into a large amount of water, giving a quantitative yield.

The infra-red (i.r.) spectrum of the polymer showed that the absorptions (1000 and 900 cm^{-1}) of the vinyl group disappeared, although the characteristic absorption around 1650 cm^{-1} was not observed due to the overlapping of the strong amido carbonyl band at 1636 cm^{-1}. This peak, as expected, shifts 12 cm^{-1} to a higher wavenumber as compared with that of monomer **1** (*Figure 1*). The resulting polymer is confirmed by ^{1}H n.m.r. to be poly[4-vinyl-(*N,N*-diisopropylbenzamide)], as shown in *Figure 2*.

The results for the anionic polymerization of **1** with several initiators are summarized in *Table 1*. The polymer yields were all quantitative. There is a good agreement between the $\bar{M}_n$ values measured by v.p.o. and calculated from the monomer to initiator ratio. The g.p.c. curves indicated that all the polymer samples possessed a very narrow molecular weight distribution. The $\bar{M}_w/\bar{M}_n$'s, calculated by Tung's method[16] using a polystyrene calibration, are in the range 1.04 to 1.06. A representative g.p.c. curve is shown in *Figure 3*. These results indicate that the anionic polymerization of **1** proceeds without any side reactions such as transfer and termination reactions.

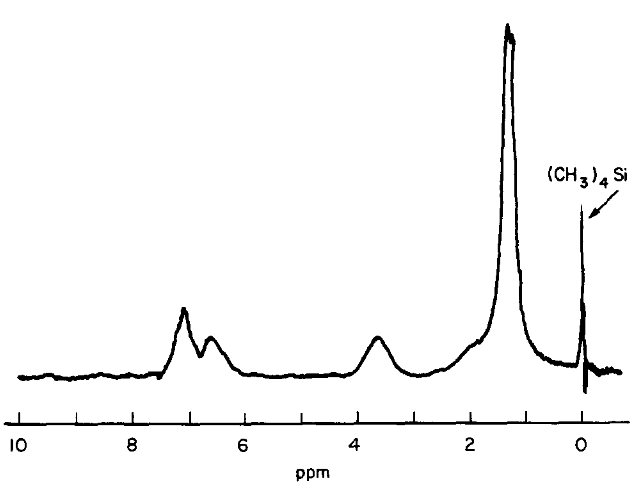

Figure 2 ^{1}H n.m.r. spectrum of poly[4-vinyl(*N,N*-diisopropylbenzamide)

Table 1 Anionic polymerization of 4-vinyl(*N*,*N*-diisopropylbenzamide) (**1**) with various initiators in THF at −78°C for 30 min

(**1**) (mmol)	Initiator (mmol)		α-Methylstyrene (mmol)	Conversion (%)	$\bar{M}_n$ calcd.[a]	$\bar{M}_n$ obsvd.[b]	$\bar{M}_w/\bar{M}_n$
3.90	Butyllithium	0.128	0.256	100	7200	6000	1.05
4.53	Cumyl potassium	0.0944	–	100	11000	10000	1.04
3.46	Potassium naphthalide	0.122	0.359	100	14000	11000	1.06
4.42	Potassium naphthalide	0.0981	0.202	96	21000	20000	1.06

[a] Calculated from the monomer to initiator ratio

[b] By v.p.o. in benzene

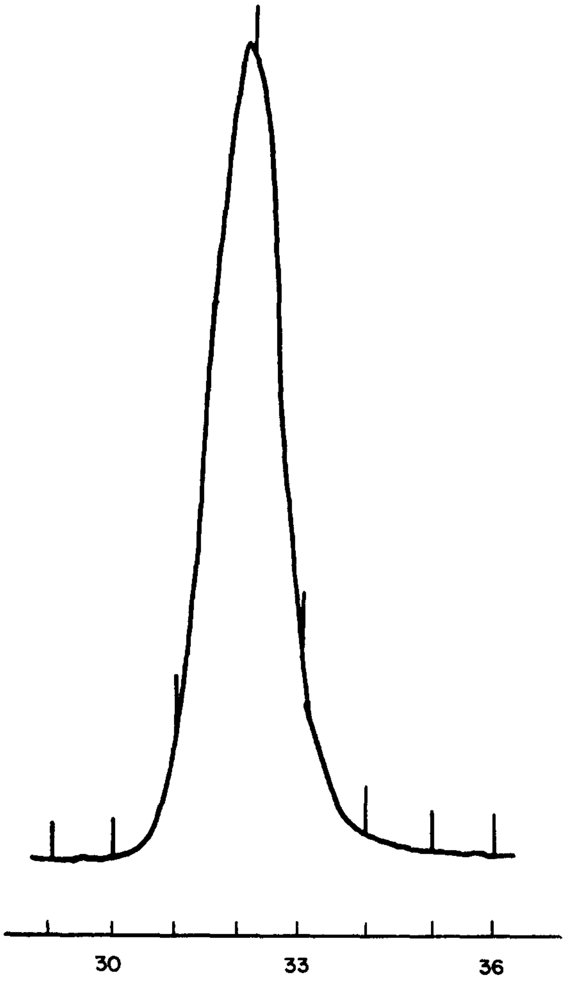

Figure 3 Molecular weight distribution for poly[4-vinyl(*N*,*N*-diisopropylbenzamide)]: $\bar{M}_n$ obsvd. (v.p.o.) = 10000

Furthermore, a rapid initiation in this system is indicated by the fact that the polymers had narrow molecular weight distributions.

The resulting polymer was a white solid soluble in a wide variety of solvents such as benzene, toluene, THF, 1,4-dioxane, diethyl ether, acetone, ethyl acetate, acetonitrile, nitromethane, pyridine, dichloromethane, chloroform, carbon tetrachloride, *N*,*N*-dimethylformamide, and even in methanol and ethanol, but insoluble in pentane, hexane, triethylamine, and water. The polymer could be cast into a transparent, colourless and brittle film from THF solution.

The polymer has a relatively high glass transition temperature (162°C), higher than those[17] of poly[4-vinyl(*N*,*N*-dimethylbenzamide)] (125°C) and poly[4-vinyl(*N*,*N*-diethylbenzamide)] (102°C).

Block copolymerization

The synthesis of block copolymers of **1** and a nonpolar monomer such as α-methylstyrene has stimulated a great deal of interest since they contain both hydrophobic and hydrophilic blocks and generally lead to heterophasic materials.

The utilization of poly(α-methylstyryl)lithium as an initiator for the polymerization of **1** results in a diblock copolymer of the AB type where the A and B blocks are poly(α-methylstyrene) and poly[4-vinyl(*N*,*N*-diisopropylbenzamide)], respectively. When **1** was added to living poly(α-methylstyrene), prepared with butyllithium in THF at −78°C, the viscosity increased and a quantitative polymer yield was obtained. The results are summarized in *Table 2* and the g.p.c. curves of the resulting polymers are shown in *Figure 4*. The block polymerization product possesses a unimodal narrow molecular weight distribution, clearly shifting towards higher molecular weight than that for the starting poly(α-methylstyrene). The composition of the block copolymer, determined by ^{1}H n.m.r., was almost the same as that calculated from the amounts of both monomers polymerized. The molecular weight of the polymer was estimated by its composition and the $\bar{M}_n$ of the starting poly(α-methylstyrene). The molecular weight value was in agreement with that expected from the monomer to initiator ratio. These results indicate that the block copolymerization proceeds efficiently without transfer and termination reactions.

In a similar manner, an attempt was made to synthesize a triblock copolymer of the type ABA by addition of α-methylstyrene to the polymeric dianion of **1**, prepared from **1** and poly(α-methylstyryl) potassium at −78°C in THF. However, α-methylstyrene did not polymerize from this polymeric dianion. The recovered polymer was found by ^{1}H n.m.r. and i.r. analyses not to include α-methylstyrene units. The g.p.c. peak of the polymer was virtually identical with that of the original polymer from **1**. Thus, the formation, by this procedure, of an ABA triblock copolymer is not successful because the carbanion obtained from **1** cannot polymerize α-methylstyrene. The reason for this would be that the electron withdrawing character of the tertiary amido carbonyl group lowered the nucleophilicity of the 4-(*N*,*N*-diisopropyl)styryl anion. A similar phenomenon has recently been reported by Königsberg and Jagur-Grodzinski[18] for the block copolymerization of 4-bromostyrene and styrene where poly(4-bromostyryl) anions, stabilized by the electron withdrawing bromine atom, do not initiate the polymerization of styrene.

This paper describes the first demonstration of the anionic living polymerization of a tertiary-amido substituted styrene. Anionic polymerization of other amido-containing monomers is presently under investigation.

Table 2 Block copolymerization of α-methylstyrene with **1** poly(α-methylstyryl)lithium[a]

Addition	α-Methylstyrene (mmol)	**1** (mmol)	Buthyllithium (mmol)	Conversion (%)	$\bar{M}_n$ calcd.	$\bar{M}_n$ obsvd.
First	26.0	–	0.170	100	18000	16000[b]
Second[c]	20.2	3.90	0.130	100	25000	22000[d]

[a] All polymerizations were carried out in THF at −78°C for 1 h (first polymerization) and for 0.5 h (second polymerization)
[b] By v.p.o. in benzene
[c] 3.90 mmol of **1** was added to a reaction mixture of 20.2 mmol of α-methylstyrene and 0.130 mmol of butyllithium
[d] Estimated from the copolymer composition by ^{1}H n.m.r. and the molecular weight of the starting poly(α-methylstyrene)

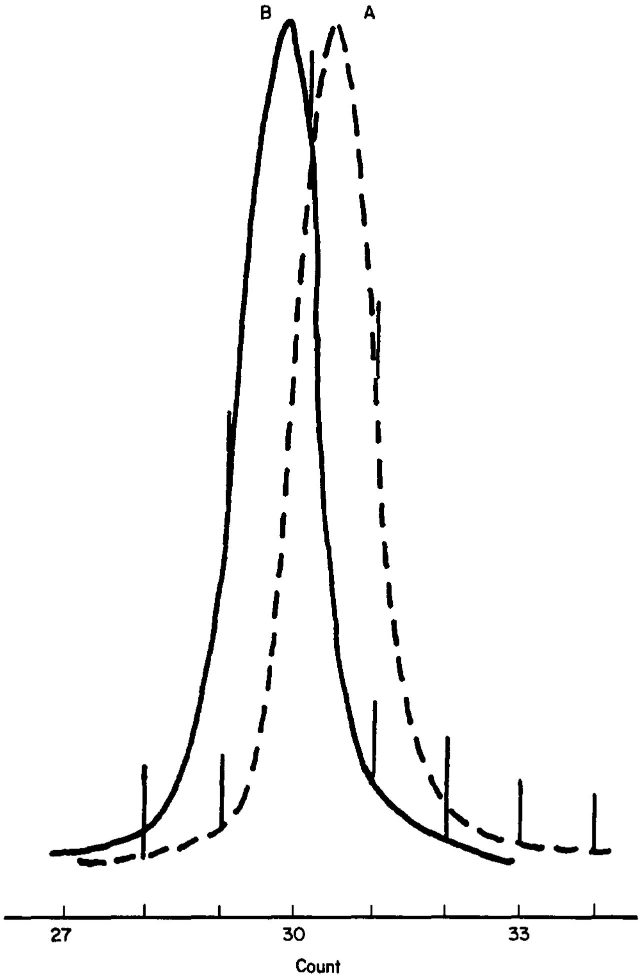

Figure 4 Molecular weight distributions for poly(α-methylstyrene) initially polymerized, (A) $\bar{M}_n$ obsvd. (v.p.o.) = 16 000; and for block copolymer, (B) $\bar{M}_n$ obsvd. = 22 000

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