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End-functionalized polymers by living cationic polymerization
3. Ring-substituted anilines as functional end-capping agents for the synthesis of poly(isobutyl vinyl ether) with a terminal amine, carboxylic acid, or ester group

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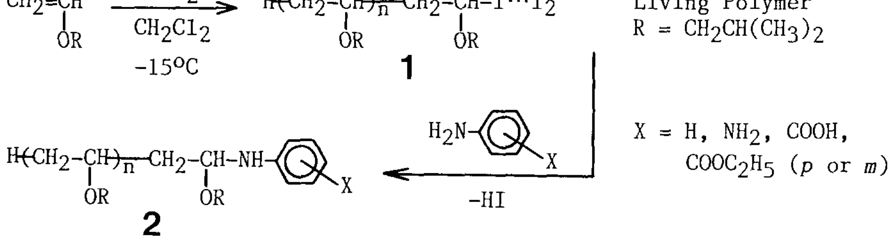
SUMMARY

End-functionalized poly(isobutyl vinyl ether) (**2**) with a terminal amine, carboxylic acid, or ester group was prepared by quenching the HI/I_2-initiated living polymer ends with ring-substituted anilines ($H_2N-C_6H_4-X$, *p* or *m*; X = NH_2, COOH, $COOC_2H_5$). The living polymerization of isobutyl vinyl ether and the subsequent end-capping reaction were carried out at -15^oC in methylene chloride. The resulting polymers exhibited a narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n$ = 1.1–1.2) and carried one terminal function (aniline residue) per chain, according to ^1H NMR structural analysis.

INTRODUCTION

In cationic polymerization of vinyl compounds, in general, amines are strong terminating agents that combine with the propagating carbocations (1). In a previous study (2), we utilized aliphatic amines to quench living poly(vinyl ethers), generated by the hydrogen iodide/iodine (HI/I_2) initiating system, for the synthesis of end-functionalized polymers. Thus, addition of an excess amount of *n*-butylamine and hexamethylenediamine to a living polymer solution led to secondary and primary amino terminals, respectively. A disadvantage of the use of aliphatic amines is that the resulting end group is an amino ether [∿∿CH(OR)-NHR'; R = alkyl, R' = H or alkyl] which is unstable except under basic conditions.

As an extension of these investigations, this study concerns the synthesis of a series of end-functionalized poly(isobutyl vinyl ether) (**2**) by the reactions of the HI/I_2-initiated living polymers (**1**) with ring-substituted anilines as "functional" end-capping agents (Scheme 1):



Scheme 1

The added anilines turned out to combine selectively with the living polymer end, without inducing β-proton elimination and other undesirable side reactions, thereby giving the target polymers (**2**) where the ring substituent X serves as a terminal functional group.

As end-capping agents the aromatic amines are expected to offer the following advantages over the aliphatic counterparts: (i) a series of ring-substituted aniline derivatives are readily available which in turn provide various terminal functions including aromatic primary amine, carboxylic acid, and its esters; (ii) the resultant aromatic amino ether terminals would be stable in a wider pH range than the corresponding aliphatic amino ethers; and (iii) the terminal benzene nucleus derived from the anilines would enable an accurate determination of the end-group structure and the number-average end functionality ($\bar{F}_n$) by ^{1}H NMR spectroscopy.

RESULTS AND DISCUSSION

Reactions of Living Poly(IBVE) with Ring-Substituted Anilines

Living poly(IBVE), initiated by the HI/I_2 system at -15°C in methylene chloride (3,4), was treated with the anilines (in acetone) in a large stoichiometric excess over the living ends. Figure 1 shows the representative MWD profiles for the polymers obtained with the *p*-substituted quenchers. All polymers showed a very narrow MWD ($\bar{M}_w/\bar{M}_n$ = 1.1-1.2; see also Table 1 below) that was nearly the same in position and narrowness as that for a control sample quenched with methanol. The MWD traces with a UV detector (254 nm) well agreed with the corresponding eluograms by refractive-index detection, which shows uniform incorporation of the aniline residue to the polymers over the whole molecular weight range. Similar results were obtained for the *m*-substituted anilines. Thus the aniline derivatives were found to effectively terminate the HI/I_2-initiated living polymerization of IBVE; the narrow MWDs of the products further indicate that the quenching reactions with the anilines are sufficiently fast.

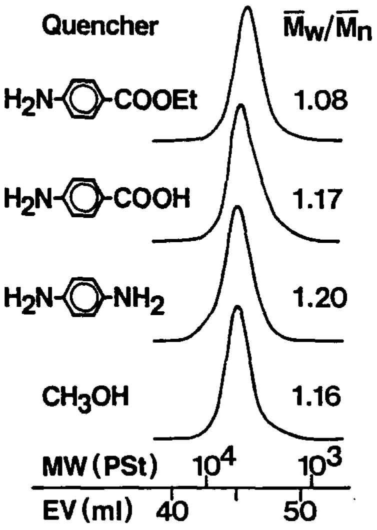


Figure 1. MWD of poly(IBVE) capped with *p*-substituted anilines or with methanol. See Table 1 for synthesis conditions.

End Group and Functionality Analysis

Figure 2 illlustrates the ^{1}H NMR spectra of poly(IBVE) obtained after quenching the living polymer ends with the seven anilines. In addition to the absorptions due to the poly(IBVE) chain (δ 0.8-4.0), the samples exhibited distinct signals in the aromatic region which are assignable to the aniline residues attached to the polymer terminal. The splitting patterns of these ring-proton resonances were consistent with the structure of the end-capping agents; e.g., for aminobenzoic acid (X = COOH) and ethyl aminobenzoate (X = $COOC_2H_5$), the chemical shift differences among the ring protons were greater for the *p*-isomers than for the *m*-isomers. The polymers capped with the aminobenzoates also showed a qualtet at δ 3.9 arising from the terminal ester methylene. Without exception signals assignable to ter-

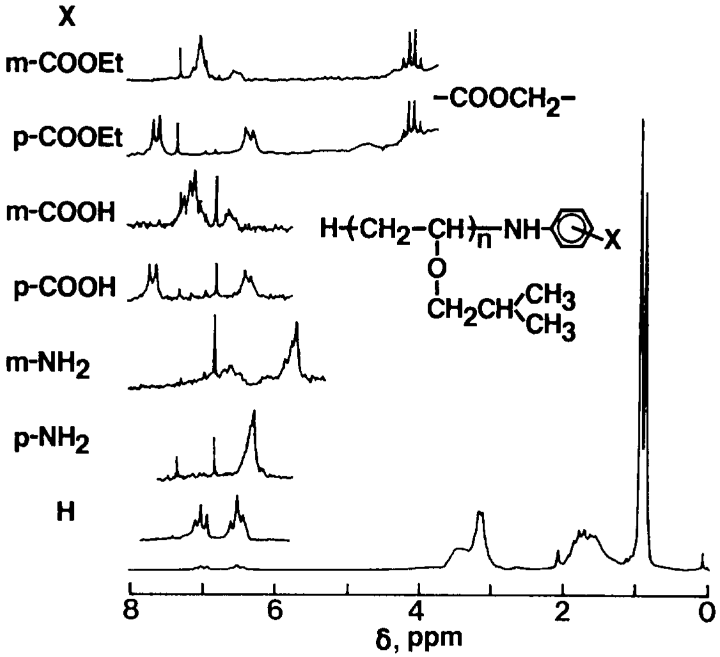


Figure 2. ^{1}H NMR spectra of poly(IBVE) capped with ring-substituted anilines. See Table 1 for synthesis conditions.

minal olefins were absent. All these spectral data demonstrate the attachment of the aniline residue at the poly(IBVE) chain end (see Scheme 1).

Close inspection of the NMR spectra revealed the existence of additional small signals at δ 2.6-2.8 (broad multiplet) and 2.15 (singlet) with the intensity ratio ca. 2:3 for most samples except those with phenylenediamines (X = NH$_2$). The latter singlet corresponded to the methyl absorption of acetone (the diluent for the aniline quenchers). On the basis of this and the authentic ^{1}H-NMR spectra of relevant model compounds (5), we tentatively attribute these signals to the terminal structure $\sim\!\sim CH_2\text{-}CH(C\mathit{H}_2\text{-}CO\text{-}C\mathit{H}_3)\text{-}NH\text{-}C_6H_4\text{-}X$ for which the broad resonance at δ 2.6-2.8 is assignable to the methylene protons adjacent to the carbonyl group; 1-diethylamino-3-butanone $[(C_2H_5)_2NCH_2C\mathit{H}_2\text{-}CO\text{-}C\mathit{H}_3]$, for example, exhibits the absorptions of the italicized methylene and methyl groups at δ 2.6-2.9 and 2.17, respectively (5).

The proposed aminoketone terminal may form via the substitution reaction of the enolate carbanion of acetone with the terminal isobutoxyl pendant of the end-capped poly(IBVE) **2** in the presence of the basic aniline quenchers. Enolate carbanions are known to form from acetone and related ketones under basic conditions (e.g., in base-promoted halogenation of ketones) (6). It should be emphasized here that even if such a terminal does form, the end functionality ($\overline{F}_n$) of the products is not affected at all.

The $\overline{F}_n$ values of the aniline-capped poly(IBVE) were then determined from the NMR spectra. Thus, the integrated signal intenity ratio of the aromatic protons to the main chain protons (δ 2.9-4.0) gave the amount (in mol/L) of the terminal aniline residues which was in turn compared with the concentration of the living end; i.e., $\overline{F}_n$ = [-NH-C$_6$H$_4$-X]/[living end] =

$[\text{-NH-}C_6H_4\text{-X}]/[\text{HI}]_0$. It has been established (3,4) for the HI/I_2-initiated living polymerization of IBVE that the living end concentration is equal to the initial hydrogen iodide concentration.

Table 1 summarizes the $\bar{F}_n$ values thus obtained together with the $\bar{M}_n$ and MWD data. All samples gave $\bar{F}_n$ values very close to unity ($\bar{F}_n = 1.0 \pm 0.1$), indicating that each polymer chain carries one terminal aniline moiety and in turn one terminal functional group X. Of particular interest is that in all cases the living polymer ends reacted selectively with the amino group of the quenchers, although these anilines (except for X = H) have two potentially basic substituents (e.g., the amino and carboxyl groups in aminobenzoic acid).

Stability of the End Groups

As pointed out in Introduction, the end-capping with the aniline derivatives leads to amino ether terminals that might be susceptible to decomposition. We thus examined the stability of the end groups of our aniline-capped poly(IBVE) as a function of the pH of the environment (see Experimental). Table 2 lists the $\bar{F}_n$ values before and after the treatment of the polymer samples with buffer solutions. The functionality values did not change in the pH range 5.00-9.18; furthermore, neither molecular weight ($\bar{M}_n$) nor narrow MWD of the polymers was affected by this treatment. These results show the high stability of the end groups (at pH > 5), which probably arising from their aromatic, rather than aliphatic, amino ether structure. For example, our separate experiments (7) for poly(IBVE) capped with benzylamine [$H(CH_2\text{-}CHOR)_n NHCH_2C_6H_5$; R = isobutyl] showed that the end functionality drops below unity after the treatment with acidic buffer solutions (see Experimental); i.e., $\bar{F}_n$ (pH): 1.04 (7.00), 0.89 (6.86), 0.21 (5.00).

In conclusion, the end-capping of the HI/I_2-generated living poly(IBVE) with ring-substituted anilines provided a series of end-functionalized polymers with a controlled molecular weight and a narrow MWD. A particular advantage of this method is that a variety of terminal functions, including amines, carboxylic acids, and their esters, can be introduced via simple one-pot procedures.

EXPERIMENTAL

Materials

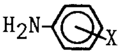
Aniline and its ring-substituted derivatives ($H_2N\text{-}C_6H_4\text{-X}$, *p* or *m*; X = NH_2, COOH, $COOC_2H_5$; Wako Chemicals, all guaranteed reagents) were of commercial source and used as received; except for aniline and ethyl *m*-aminobenzoate, the solid materials were dried in vacuo for 2 h before use. Isobutyl vinyl ether (IBVE) was washed sequentially with 10% aqueous sodium hydoxide solution and with water, dried overnight with potassium hydroxide pellets, doubly distilled over calcium hydride, and sealed in ampules under dry nitrogen. Anhydrous hydrogen iodide (*n*-hexane solution) and iodine were obtained as reported (3). Methylene chloride as polymerization solvent was purified by the usual methods (3) and distilled twice over phosphorus pentoxide and then over calcium hydride just prior to use. Acetone (diluent for the anilines) was doubly distilled over calcium hydride.

Procedures

Living polymerization of IBVE by the HI/I_2 initiating system was carried out under dry nitrogen in methylene chloride solvent at -15°C ($[\text{IBVE}]_0 = 0.38$ M (5.0 vol%), $[\text{HI}]_0 = 10\text{-}12$ mM, $[I_2]_0 = 0.20$ mM; polymerization solution, 5.0 mL) (4). When the reaction reached near completion in 15 min,

Table 1

End-Capping Reactions of Living Poly(IBVE) with Ring-Substituted Anilines[a]

 X	$[HI]_0$, mM	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	$\bar{F}_n$[b]
m-$COOC_2H_5$	12	3400	1.07	0.98
p-$COOC_2H_5$	12	3400	1.08	1.00
m-COOH	10	3200	1.12	1.10
p-COOH	10	3900	1.17	0.92
m-NH_2	11	3500	1.16	0.95
p-NH_2	10	4500	1.20	1.01
H	12	3200	1.09	1.02
CH_3OH	10	4200	1.16	—

a) Polymerization by HI/I_2 in methylene chlolride at -15°C; $[IBVE]_0$ = 0.38 M, $[I_2]_0$ = 0.20 mM, conversion ∼100%.
b) $\bar{F}_n = [-NH-C_6H_4-X]/[HI]_0$; by ^1H NMR.

Table 2

Stability of Aniline-Capped Poly(IBVE)[a]

pH	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	$\bar{F}_n$[b]
5.00	3300	1.07	0.99
6.86	3300	1.07	1.01
7.00	3100	1.07	1.00
9.18	3200	1.07	1.03
Untreated	3100	1.08	1.05

a) End group: $-NH-C_6H_5$ (X = H); at 30°C for 24 h; see Experimental for procedures.
b) $\bar{F}_n = [-NH-C_6H_5]/[HI]_0$; by ^1H NMR.

a solution or suspension of the anilines in acetone (1.0 g/5.0 mL; $[-NH_2]/[\text{living end}] = 60\text{-}110$) was added to quench the living polymers. For control runs, the polymerization was terminated with prechilled ammoniacal methanol (2.5 mL). The quenched reaction mixtures were diluted with methylene chloride (15 mL), washed with 10% aqueous sodium thiosulfate solution and then with water for removal of the inorganic residues, evaporated to dryness under reduced pressure, and vacuum dried overnight to give the products, which were then subjected to preparative size-exclusion chromatography (Jasco Megapak polystyrene gel 201; 2.0 cm i.d. x 50 cm) in chloroform to remove the unreacted aniline quencher.

The molecular weight distribution (MWD), number-average molecular weight ($\bar{M}_n$), and polydispersity ratio ($\bar{M}_w/\bar{M}_n$) of the isolated polymers were determined by size-exclusion chromatography in chloroform on a Jasco Trirotar-II instrument equipped with three polystyrene gel columns (Shodex A-802, A-803, A-804; 0.8 cm i.d. x 50 cm each) on the basis of a polystyrene calibration. ^1H NMR spectra were recorded in $CDCl_3$ at room temperature on a Joel FT-90Q spectrometer.

The stability of the aniline-capped polymer (**2**, X = H, Scheme 1) was studied as follows. In a 50-mL beaker, a solution of the polymer in *n*-hexane (100 mg/10 mL) and a standard aqueous phosphate buffer solution (10 mL; pH = 5.00, 6.86, 7.00, or 9.18) were magnetically stirred at ca. 30°C for 24 h. The organic phase was then separated, evaporated to dryness, and vacuum dried overnight. The polymers thus recovered was analyzed by size-exclusion chromatography and ^1H NMR spectroscopy.

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