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Dendritic polymers from vinyl ether

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Summary

1-[(2-Vinyloxy)ethoxy]ethyl acetate (1) was prepared by the addition reaction between ethylene glycol divinyl ether and acetic acid. 1 contains both a cationically polymerizable C=C double bond and a dormant initiating moiety for cationic polymerization. It can, therefore, undergo self condensing cationic polymerization in the presence of a Lewis acid activator, such as zinc chloride. Using this procedure, a novel dendritic polymer consisting of vinyl ether was prepared and its hyperbranched molecular structure confirmed by FT-IR and ^{1}H NMR spectra.

Introduction

The dendritic polymers have received increased attention in recent years, because of their quite different macromolecular architecture compared to that of the traditional linear polymers, and of their unusual properties (1-4). The special hyperbranched structure and unique properties of these polymers can be exploited to design novel polymer materials which possess unique viscoelastic properties (5, 6), can form unusual blends (7, 8) and can be employed as molecular carriers (9, 10).

The dendritic polymers were generally prepared step by step using both divergent and convergent methods (11, 12). However, these complex multistep procedures limit the capability for preparing the dendritic polymers. Recently, Fréchet and his coworkers (13, 14) developed a convenient method, called self condensing vinyl polymerization, to prepare dendritic polymers with broad molecular weight distributions. They employed a vinyl monomer, 3-(1-chloroethyl)-ethenylbenzene, which, containing both a polymerizable C=C double bond and a dormant initiating moiety, can undergo self condensation in the presence of an activator ($SnCl_4$) to generate a dendritic polymer. Several styrene type den-

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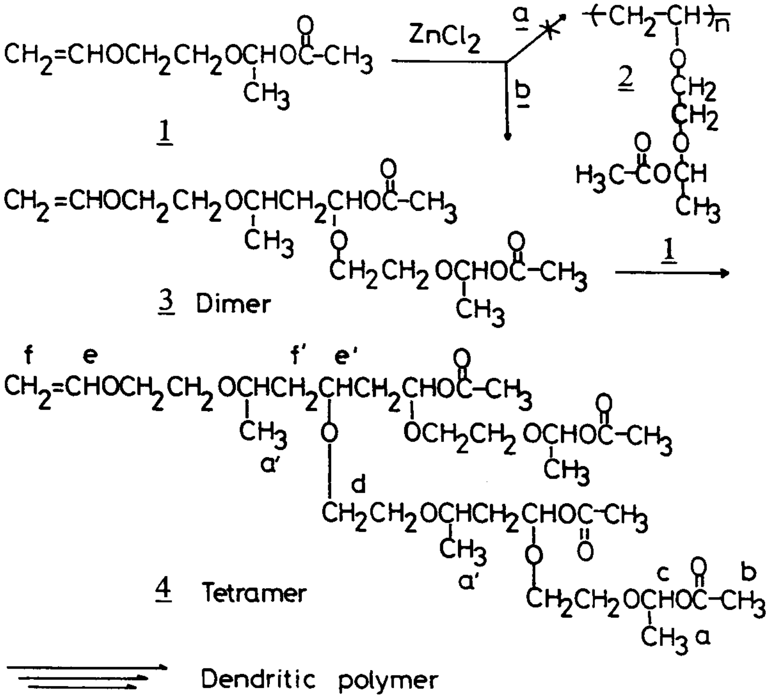
Scheme 1



dritic polymers were thus prepared (13, 14).

Higashimura and coworkers (15, 16) found that the adduct between an alkyl vinyl ether and an acetic acid derivative (RCOOH, R=CF_3, CCl_3, $CHCl_2$, CH_2Cl, CH_3) can be used as initiator for the living cationic polymerization of vinyl ether in the presence of $ZnCl_2$. This suggested to us to prepare a novel dendritic polymer based on vinyl ether. The vinyl monomer, 1-[(2-vinyloxy)ethoxy]ethyl acetate (1; in Scheme 1), which is an adduct between ethylene glycol divinyl ether and acetic acid, was first prepared. 1 contains both a cationically polymerizable C=C double bond and an initiating moiety, whose structure is similar to that of the initiating moiety in the cationic polymerization carried out by Higashimura et al. (15, 16). The initiating moiety of 1 can be activated by a Lewis acid ($ZnCl_2$) to give a partly dissociated carbocation which is able to initiate the cationic polymerization of the vinyl groups. There are two possible routes for the polymerization of 1. As shown in Scheme 1, route a provides a linear polymer (2). In this case, 1 acts just as a monomer. According to route b, 1 undergoes a self condensing polymerization. One initiating moiety reacts with the double bond of another 1 molecule to form a dimer (3) which, having one double bond and two reactive initiating moieties, can further react with the initiating moieties and/or the double bonds of other molecules. If it just reacts with the two double bonds of 1, a tetramer (4) will be produced. Further condensations involving the activated 1, dimers and oligomers, will generate a highly branched dendritic polymer. In this paper, the polymerization of 1 was proved to proceed according to route b.

Experimental

Materials

Toluene (solvent) was washed with concentrated sulfuric acid, then with water, dried over $MgSO_4$ and distilled twice over calcium hydride just before use. Et_2O was dried with CaH_2 and distilled in the presence of $LiAlH_4$. $ZnCl_2$ (Aldrich, 1.0M solution in diethyl ether) was diluted with purified Et_2O.

Synthesis of 1-[(2-vinyloxy)ethoxy]ethyl acetae (1)

1 was prepared through the reaction between ethylene glycol divinyl ether (EGDE; Aldrich, 97%) and acetic acid (AA; Aldrich, 99.8%). AA (22.2g, 0.37mol) was dropwise added to EGDE (45.7g, 0.39mol) with magnetic stirring at 60°C and kept at this temperature for 8h. The pure 1 was obtained as a colorless oil by careful distillation under reduced pressure.

Polymerization procedure

The polymerization was carried out in a 100 mL round-bottom glass flask, under nitrogen, with magnetic stirring. The reaction was initiated by adding a Et_2O solution of $ZnCl_2$ to a solution of 1 with a dry syringe, at a selected temperature. The polymerization was terminated with methanol (ca. 2mL) containing a small amount of ammonia.The quenched reaction mixture was washed with 10 wt% aqueous sodium thiosulfate solution and then with water, evaporated to dryness under reduced pressure, and vacuum dried to obtain the product polymer.

Measurements

^1H NMR spectra were recorded in $CDCl_3$ on a VXR-400 spectrometer. The $\overline{M}_n$ and $\overline{M}_w/\overline{M}_n$ of the polymer were determined by gel permeation chromatography (GPC) on the basis of a polystyrene calibration. The GPC measurements were carried out with tetrahydrofuran as solvent, at 30°C, using two polystyrene gel columns (Waters, Linear) connected to a Waters 515 precision pump. FT-IR spectra were recorded on a PERKIN-ELMER 1760-X spectrometer. The thermogravimetric analysis was carried out with a PERKIN-ELMER-7 instrument using a heating rate of 10°C/min.

Results and discussion

1-[(2-vinyloxy)ethoxy]ethyl acetate (1) is an adduct between ethylene glycol divinyl

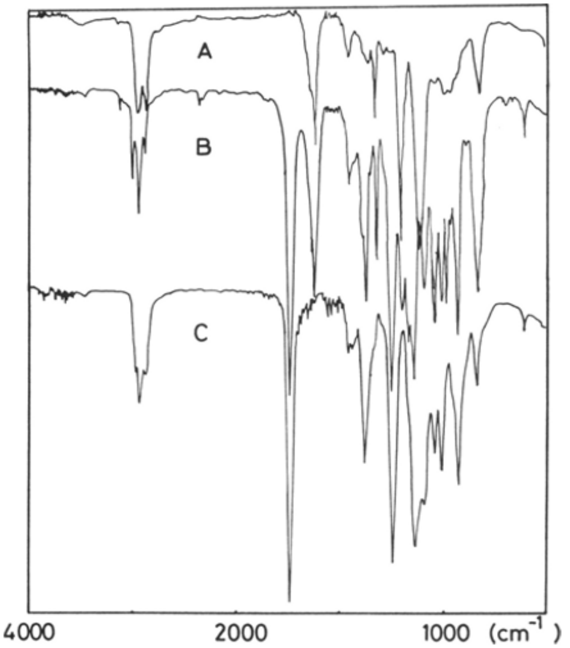


Fig. 1 FT-IR spectra of EGDE (A), 1 (B) and the dendritic polymer of 1 (C; no. 1 in Table1)

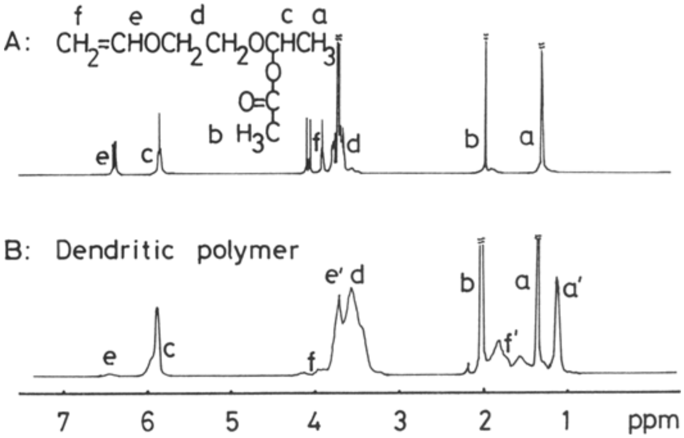


Fig. 2. ^{1}H NMR spectra of 1 (A) and the dendritic polymer of 1 (B; refers to the molecular structure of tetramer in Scheme 1). The polymerization was carried out in toluene at 0°C for 60 min. [1]=0.57M, [ZnCl$_2$]=6.3mM.

Table 1: Preparation of a dendritic polymer from 1 in toluene

No.	$[1]_0$ M	$[ZnCl_2]$ mM	Temp. ^0C	Time h	Conv. %	$10^{-3}\overline{M}_w$[a]	$10^{-3}\overline{M}_n$[a]	$\overline{M}_w/\overline{M}_n$[a]
1	0.57	25.0	0	24	96	44.3	4.51	9.8
2	0.57	12.5	0	24	95	23.4	4.32	5.4
3	0.57	12.5	20	24	99	27.3	3.50	7.8
4	0.22	2.0	0	42	91	32.6	3.80	8.6

[a]Determined from GPC measurements based on a polystyrene calibration.

ether (EGDE) and acetic acid (AA). However, the reaction between EGDE and AA generates not only 1, but also a by-product between one EGDE and two AA molecules, as well as some unreacted EGDE. In the polymerization of 1, the presence of the unreacted EGDE results in gelation because EGDE ($CH_2=CHOCH_2CH_2OCH=CH_2$) has two double bonds. This was proved by mixing 1 with EGDE in the proportion 9/1 wt/wt. The polymerization of this mixture in the presence of $ZnCl_2$ produced a gel which could not be dissolved in any solvent. It is, therefore, necessary to separate 1 from the reaction mixture carefully. This was carried out by many successive distillations under reduced pressure. Just prior to polymerization, 1 was again doubly distilled in the presence of CaH_2. A 40% yield based on AA was achieved (bp: 41°C at 0.1mmHg; purity>99%). Comparing the FT-IR spectrum of the prepared 1 (B, Fig. 1) with that of EGDE (A, Fig. 1), one can note the presence of the carbonyl stretching band at 1739 cm^{-1}. As shown in Fig. 2-A, the chemical shifts and their intensities in the ^1H NMR spectrum of the prepared 1 are consistent with its molecular structure.

The polymerization of 1 was carried out in the presence of $ZnCl_2$ in toluene at 0 or 20°C. After adding $ZnCl_2$ to the toluene solution of 1, the polymerization system was transparent. As the polymerization proceeded, a red color appeared sometimes gradually, depending on the concentration of $ZnCl_2$ and the polymerization temperature. For instance, when $[ZnCl_2]$=25.0mM at 0°C (no.1, Table 1), the red color emerged after 5 h. At the same temperature, but for $[ZnCl_2]$=12.5mM (no. 2, Table 1), it took 12 h. When the polymerization temperature was raised to 20°C (no. 3, Table 1), the red color appeared after 8 h. If the concentration of $ZnCl_2$ was too low (no. 4, Table 1), no color change was observed during polymerization.

As depicted in the GPC traces of Fig. 3, during the initial period, low molecular weight oligomers (b) were formed from 1 (a). Then, the condensation generated gradually high molecular weight dendritic polymers (c). At the same concentration of 1 (no. 1 to 3, Table 1), the higher the concentration of $ZnCl_2$ or the temperature, the larger the weight-average molecular weight and the broader the molecular weight distribution. Table 1 and Fig. 3 show that the molecular weight distributions of the dendritic polymers are broad ($\overline{M}_w/\overline{M}_n$=5.4-9.8). This is mainly due to the self condensing vinyl polymerization (13), which because of its complex propagation provides dendritic polymers with broad molecular weight distributions. In addition, the broad molecular weight distribution can be also related to the structure of 1. According to Higashimura et al. (15, 16), in the cationic polymerization of vinyl ethers initiated by $CH_3CH(OiBu)OCOR$, a broad molecular weight distribution is obtained when R=CH_3. The effect of the monomer structure on the molecular weight distribution of the dendritic polymer is now investigated by using the monomer $CH_2{=}CHOCH_2CH_2OCH(CH_3)OCOCF_3$.

The dendritic polymer obtained is soluble in methanol, acetone, acetic acid, ethyl ether, tetrahydrofuran, benzene, toluene, dichloromethane, chloroform, carbon tetrachlo-

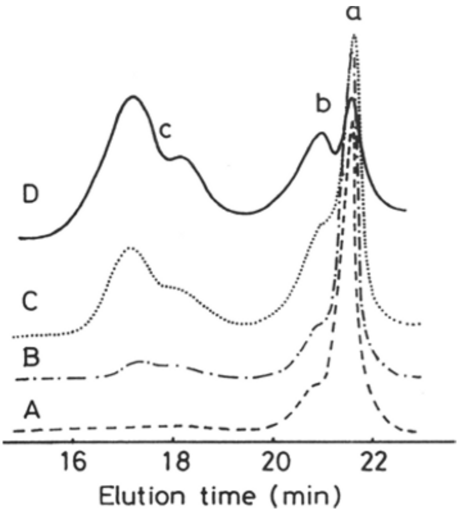


Fig. 3 GPC traces of the oligomers and dendritic polymers of 1 at various reaction times. Polymerization in toluene at 0°C for 5 min (A), 45 min (B), 3.5 h (C) and 23 h (D), $[1]_0$=0.22M, $[ZnCl_2]$=2.0mM. Peak a: 1, peak b: oligomers, peak c: dendritic polymers.

ride, N, N-dimethylformamide and methyl sulfoxide, but is insoluble in water, 1-butanol, hexane and cyclohexane. As shown in Fig. 1, the absorption of C=C double bond in 1 (B) at 1638 cm^{-1} almost disappeared in the IR spectrum (C) of the dendritic polymer, indicating that only a trace amount of C=C double bonds remained unreacted.This trace amount arises because each molecule of the dendritic polymer possesses one double bond (see Scheme 1). This result is consistent with the ^1H NMR measurements. As shown by Fig. 2, very weak absorptions of CH_2=CH double bonds (f, e) can still be detected. The obvious evidence for the formation of the dendritic polymer is that the absorption at 1.37ppm (a) of methyl in 1 was split into two peaks a (1.37 ppm) and a′ (1.14 ppm) after polymerization, corresponding to the methyls (a′) inside the molecules and those (a) at the periphery of the dendritic polymer, respectively (see the molecular structure of the tetramer in Scheme 1). It was, furthermore, observed that the intensity of the absorption a′ increased gradually as the polymerization proceeded. If the polymerization would have proceeded by route a (Scheme 1), the peak a′ would have had to be absent in the ^1H NMR spectrum. These results indicate that the polymerization of 1 proceeded according to route b (Scheme 1) and that a dendritic polymer with hyperbranched structures was indeed obtained.

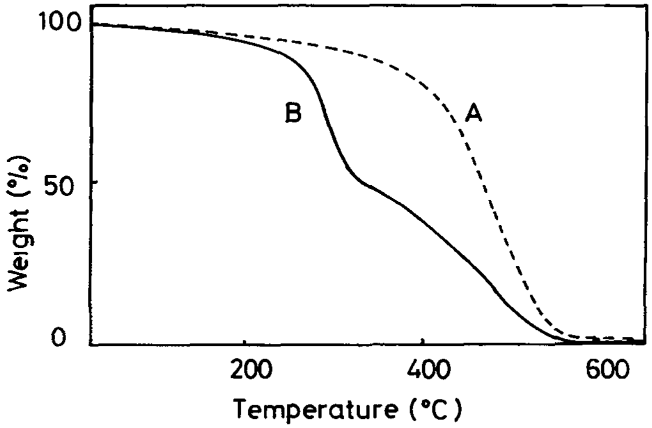


Fig. 4 Thermogravimetric curves of poly(VEE) (A; Aldrich, Catalog No. 18265-6) and the dendritic polymer of 1 (B; no. 1 in Table 1)

Fig. 4 presents the thermogravimetric curve (B) of the dendritic polymer. For comparison, the thermogravimetric curve (A) of poly(vinyl ethyl ether) (PVEE) is also depicted. The decomposition of PVEE exhibits one step from 421 to 558°C, corresponding to the decomposition of the carbon-carbon main chain. However, the decomposition of the dendritic polymer is much more complicated. The first step from 259 to 314°C can be attributed to the groups ($CH_3CHOCOCH_3$) at the periphery (see the molecular structure of the tetramer in Scheme 1). The second step from 314 to 545°C can be attributed not only to the carbon-carbon, but also to the carbon-oxygen chains, and for this reason the decomposition temperature is lower than that of the linear PVEE. These results also confirm the complicated molecular structure of the dendritic polymers obtained from 1.

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