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Synthesis of poly(t-butyl acrylate) macromer with vinyl ether functionality by metal-free anionic polymerization

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The anionic polymerization of t-butyl acrylate was achieved by using ethyl vinyl ether functionalized carbanionic initiator. In this way, poly(t-butyl acrylate) macromer with vinyl ether functionality was obtained. The macromer structure was characterized with the aid of ^{1}H nuclear magnetic resonance spectroscopy and gel permeation chromatography.

(Keywords: metal-free anionic polymerization; macromer; t-butyl acrylate)

Introduction

Ionic living polymerizations are widely used for the direct synthesis of macromers[1]. This is mainly because the ionic polymerization proceeds without spontaneous termination or transfer. In this way, adequate control of molecular weight and polydispersity, and quantitative functionalization can be achieved. Recently, metal-free carbanion initiators have been used for controlled synthesis of acrylate polymers at room temperature by Reetz *et al.*[2,3] and others[4,5]. The initiation of the polymerization by resonance stabilized carbanions with tetrabutyl ammonium ion as counterion is considered to be quantitative and the polymerization proceeds without any side reactions. This polymerization technique has been utilized to synthesize macromers having oxazoline and dicarboxyl groups as chain ends[4,6]. In this work, we employed functional carbanion initiator for the polymerization of t-butyl acrylate. In this way, poly(t-butyl acrylate) macromer having ethyl vinyl ether functionality was obtained.

Experimental

Materials. t-Butyl acrylate (Aldrich) was passed through a column of neutral alumina and then distilled over calcium hydride nitrogen atmosphere prior to use. 2-Chloroethyl vinyl ether (Aldrich) was purified by distillation. Tetrahydrofuran (THF, Merck) was dried over potassium hydroxide, distilled over sodium wire and finally distilled over sodium/benzophenone ketyl prior to use. Tetrabutyl ammonium bromide (Aldrich 99.9%) was dried over P_2O_5 and was used without further purification. Sodium hydride (80 wt% dispersion in mineral oil) (Aldrich) was used as received. Diethyl malonate was fractionally distilled under reduced pressure.

Synthesis of ethyl (2-vinyloxy) ethyl malonate. Ethyl(2-vinyloxy) ethyl malonate (EVEM) was prepared according to a procedure described by Sawamoto *et al.*[7]. A typical procedure is as follows. Sodium metal (6.3 g, 0.27 mol) was dissolved in absolute ethanol at room temperature in a three-necked, round-bottomed flask equipped with a reflux condenser. Ethyl malonate (38 ml, 0.25 mol) and 2-chloroethyl vinyl ether (50 ml, 0.50 mol) were added in this order at room temperature. The solution was refluxed for 5 h, and cooled to room temperature. The resulting heterogeneous mixture was evaporated and the residue was diluted with ether. Sodium chloride in the residue was filtered off and the organic layer was washed with 10% sodium chloride solution, dried with sodium sulfate, and concentrated by evaporating off the ether and unreacted 2-chloroethyl vinyl ether under reduced pressure (40 torr). The condensed solution was distilled at 90°C (17 torr) to remove unreacted ethyl malonate and then twice distilled *in vacuo* over calcium hydride to give ethyl(2-vinyloxy) ethyl malonate as colourless oil: yield ca. 25%; b.p. 106°C (5 torr). ^{1}H n.m.r. (chloroform-d_1): $\delta=6.3$ (dd, 1H, OCH=), $\delta=4.2$ (dd, 1H, CH=CHO, anti, overlapping with the $COOCH_2$ signal), $\delta=3.8$ (dd, 1H, CH=CHO, syn), $\delta=3.55$ (t, 1H, $CH(COOC_2H_5)$), $\delta=3.4$ (t, 2H, $CH_2OCH=$), $\delta=2.3$ (d, 2H, OCH_2CH_2-CH), $\delta=1.14$ (t, 6H, CH_3). I.r. (neat) 1635, 1612 (C=C) cm^{-1} and 1735 (C=O) cm^{-1}.

Synthesis of tetrabutylammonium ethyl(2-vinyloxy) ethyl malonate. In a 100 ml three-necked flask equipped with reflux condenser and nitrogen inlet was placed 0.145 g (4.8 mmol) sodium hydride (80 wt% dispersion in mineral oil); it was washed with two 50 ml portions of dry hexane to remove mineral oil, and dried under reduced pressure. THF (80 ml) and EVEM (1 ml, 4.8 mmol) were added respectively. After evaluation of hydrogen, tetrabutylammonium bromide (1.6 g, 5 mmol) was added and the mixture was stirred overnight at room temperature. The resulting yellow heterogeneous mixture was filtered under nitrogen and evaporated to remove THF and unreacted EVEM under reduced pressure. The oily product was obtained in 61% yield.

Polymerization of t-butyl acrylate. Tetrabutylammonium ethyl(2-vinyloxy) ethyl malonate (1.23 g, 2.6 mmol) was dissolved in 25 ml of dry THF contained in a 100 ml three-necked flask equipped with a reflux condenser, a thermometer, and a rubber septum. Monomer (2.5 ml, 17 mmol) was diluted with 12.5 ml of THF and added dropwise via a hypodermic syringe over a period of 10 min. After a spontaneous exotherm was observed, the

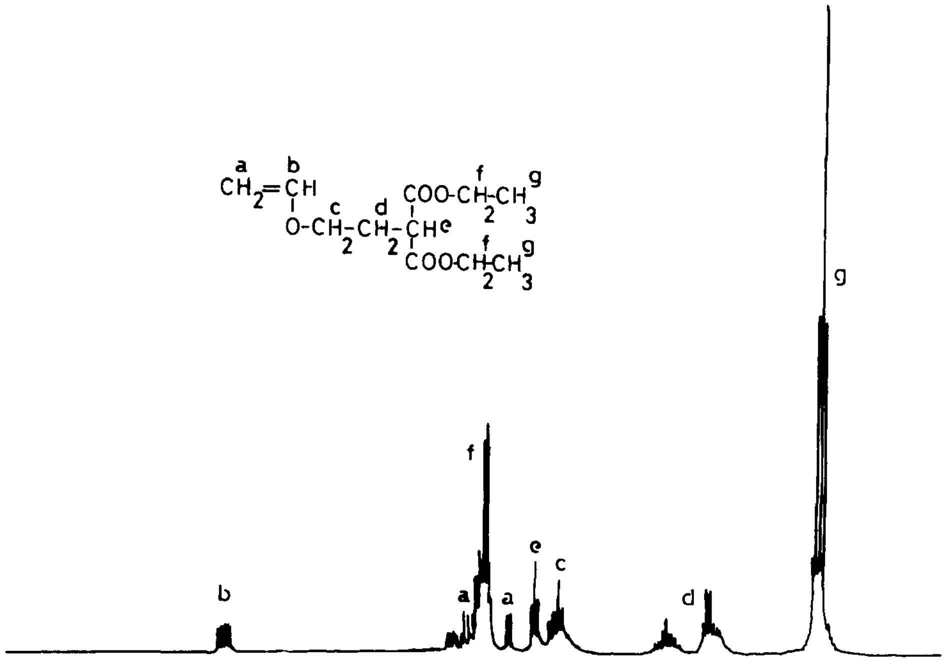


Figure 1 ^1H n.m.r. spectra of ethyl (2-vinyloxy) ethyl malonate in $CDCl_3$

polymerization continued for 3 h, and was then terminated by methanol. The quenched reaction solution was evaporated to dryness under reduced pressure. The resulting residue was dissolved in chloroform and washed with water. The chloroform layer was dried and evaporated under reduced pressure, and finally vacuum-dried to give the product polymer in 96% yield.

Measurements. ^1H n.m.r. spectra were recorded on a Bruker 200 instrument in $CDCl_3$ solution using tetramethylsilane as internal standard. G.p.c. analysis was performed with a set-up consisting of a Waters pump (model 600 E) and three Ultrastyragel columns with porosities 10^4, 500, 100 Å, respectively. THF was used as eluent at a flow rate of 1 ml min^{-1} and detection was achieved with a Waters differential refractometer (model 410). The molecular weight of the polymer was calculated with the aid of polystyrene standards. I.r. spectra were recorded on a Jasco 5300 FT-IR spectrophotometer.

Results and discussion

EVEM was prepared by the reaction of 2-chloroethyl vinyl ether with sodiomalonic ester and characterized by ^1H n.m.r. and i.r. spectroscopy. The ^1H n.m.r. spectrum of EVEM (*Figure 1*) exhibits a signal at 6.3 ppm

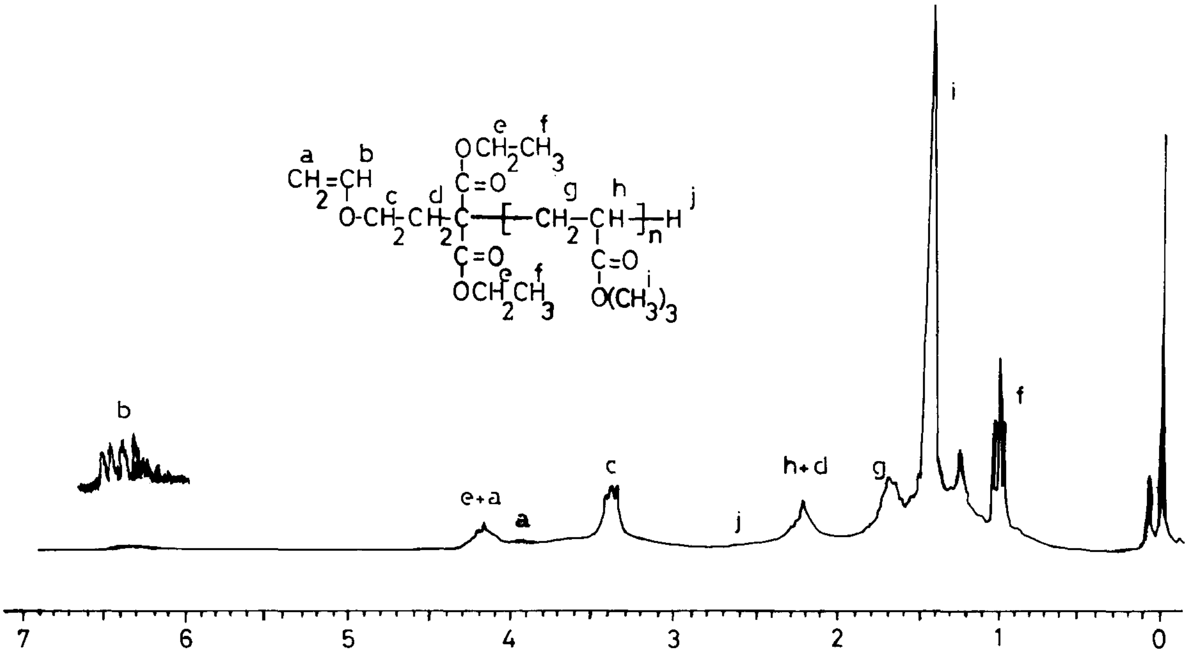


Figure 2 ^1H n.m.r. spectra of poly(t-butyl acrylate) macromer in $CDCl_3$

Table 1 Molecular weights of poly(t-butyl acrylate) macromer[a]

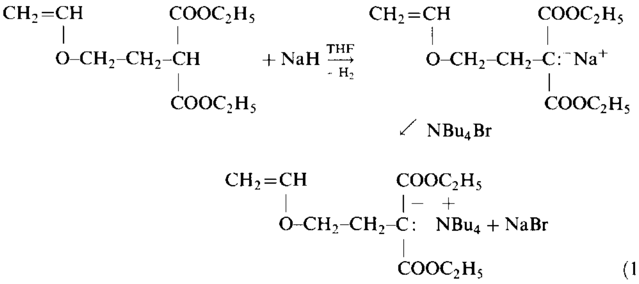
Method of determination	M_n
G.p.c.	1100
^1H n.m.r.	910[b]
Calculated	1190[c]

[a] See text for the polymerization condition

[b] Molecular weight of initiator (229 g mol^{-1}) has been added

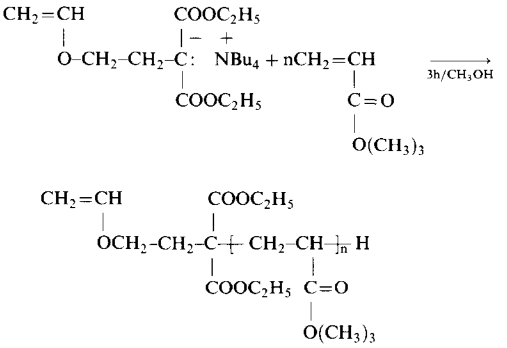
[c] M_n = (g of monomer/mol of initiator) + initiator fragment molecular weight (229 g mol^{-1})

corresponding to the OC<u>H</u>= proton of the vinyl ether in addition to characteristic signals of ester protons. The peak at $\delta = 3.55$ is assigned as the C<u>H</u>($COOC_2H_5$) proton. The i.r. spectrum of EVEM displays ester carbonyl at 1735 cm^{-1}, carbon–carbon double bond at 1635 cm^{-1}, and ether bond at 1120 cm^{-1}. EVEM was converted to the corresponding anion according to reaction (1):



$$CH_2{=}CH{-}O{-}CH_2{-}CH_2{-}CH(COOC_2H_5)_2 + NaH \xrightarrow[-H_2]{THF} CH_2{=}CH{-}O{-}CH_2{-}CH_2{-}\overset{-}{C}(COOC_2H_5)_2\,Na^+ \xrightarrow{NBu_4Br} CH_2{=}CH{-}O{-}CH_2{-}CH_2{-}\overset{-}{C}(COOC_2H_5)_2\,\overset{+}{N}Bu_4 + NaBr \qquad (1)$$

The carbanionic initiator formed in this way is capable of initiating the polymerization of t-butyl acrylate at room temperature as depicted below:



$$CH_2{=}CH{-}O{-}CH_2{-}CH_2{-}\overset{-}{C}(COOC_2H_5)_2\,\overset{+}{N}Bu_4 + nCH_2{=}CH{-}C({=}O){-}O(CH_3)_3 \xrightarrow{3h/CH_3OH} CH_2{=}CH{-}OCH_2{-}CH_2{-}C(COOC_2H_5)_2{-}[CH_2{-}CH(C{=}O{-}O(CH_3)_3)]_n{-}H \qquad (2)$$

Notably, initiation of polymerization was exothermic and there was no induction period. The composition of the macromer was determined from ^1H n.m.r. spectroscopy. As can be seen in *Figure 2*, the signals at 2.22, 1.7 and 1.44 ppm can be assigned as methyne, methylene and tertier hydrogens of the resulting polymer, respectively. Moreover, the signals at 6.3, 4.2 and 1 ppm correspond to =C<u>H</u>O, COOC$\underline{H_2}$ and methyl protons of the vinyl ether end group. Even more convincing evidence for the presence of the vinyl ether group was obtained from the complete disappearance of the signal at 3.55 ppm which is assigned as the C<u>H</u>($COOC_2H_5$) proton of EVEM. The molecular weight of the polymer is calculated from the ^1H n.m.r. spectrum (*Figure 2*) by assuming that two methyl groups are present per poly(t-butyl acrylate) molecule. The protons due to the methyl groups and to t-butyl groups of the backbone were integrated and compared. The data obtained on characterization of poly(t-butyl acrylate) with vinyl ether end group are collected in *Table 1*. As can be seen from these values, there is satisfactory agreement between the molecular weights obtained by all methods. These results clearly indicate that initiation is quantitative and proceeds by addition to monomer without any undesirable side reaction.

In conclusion, this work demonstrates that by using vinyl ether functional carbanionic initiator, poly(t-butyl acrylate) macromer with vinyl ether functionality may be prepared by taking advantage of the living nature of metal-free anionic polymerization. Utilization of this macromer provides a versatile method for preparing graft copolymers which cannot be obtained by conventional methods. Further work on the application of the resulting macromer in graft copolymerization is now in progress.

Acknowledgement

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