Polymer Bulletin 13, 447–451 (1985)

Polymer Bulletin

Synthesis of Poly(2-Methyl-2-Oxazoline) Macromers

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SUMMARY

Poly(2-methyl-2-oxazoline) (polyMeOZO) macromers having a styryl group as polymerizable function have been prepared via two methods. The first one is to use an amine nucleophile having a styryl group to terminate the living cationic propagating species of MeOZO initiated by MeOTs (1), giving rise to a macromer (2) ("terminator method"). The second one is to induce the cationic ring-opening polymerization of MeOZO by an initiator of iodomethylstyrene to give a macromer (3)("initiator method"). These macromers 2 and 3 can be used as a comonomer for the synthesis of copolymers with MeOZO graft chains.

INTRODUCTION

Macromolecular monomers (macromers as a registered name) provide a versatile method to prepare graft copolymers of well-defined structures (1). The structure and length of the graft chain can be controlled more readily at the stage of the macromer preparation than at the stage of the conventional grafting on polymer chains. In most cases, macromers have vinyl or styryl groups as a polymerizable group. Very recently, however, we have reported a ring-opening polymerizable poly(ethylene oxide) macromer having a 2-oxazoline group (2). Graft copolymers of poly[(2-phenyl-2-oxazoline)-*g*-(ethylene oxide)] derived from the macromer showed a very effective surfactant nature (3). The present paper describes preliminary results of the synthesis of macromers via ring-opening polymerization of 2-methyl-2-oxazoline (MeOZO), which possess a polymerizable styryl group.

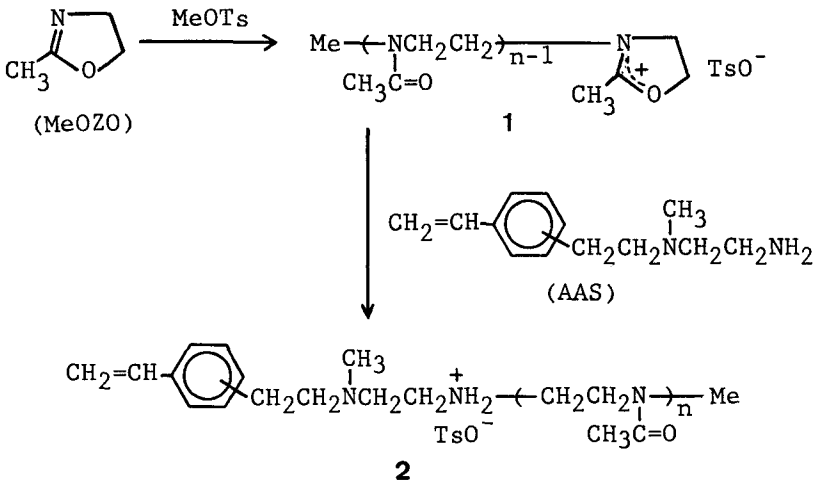
RESULTS AND DISCUSSION

Synthesis of poly(2-methyl-2-oxazoline)(polyMeOZO) macromers has been performed by two methods. The first one is based on the living nature of the MeOZO polymerization; the living cationic propagating species of MeOZO is terminated (end-capped) with an amine having a styryl group ("terminator method"). The second one is to employ an initiator having a styryl group to induce the polymerization of MeOZO ("initiator method").

Terminator Method

Cationic polymerization of MeOZO initiated by methyl p-toluenesulfonate(MeOTs) provides a system involving highly stable propagating species. This allows the preparation of di-block and multi-block type copolymers of 2-oxazolines, which are a nonionic polymeric surfactant consisting of hydrophilic and lipophilic block chains (4). The propagating species are very reactive toward certain nucleophiles such as an amine. By utilizing this nature, we have prepared a group of new surfactants by

terminating the living species of MeOZO with an amine, e.g., n-dodecyl amine and n-heptafluorobutyl amine, in which the MeOZO chain acts as a hydrophilic group whereas the amine component as a lipophilic one (5). Here, an amine of styryl type, 2-(N-2-aminoethyl-N-methyl)aminoethylstyrene (AAS), has been used to terminate the living species of MeOZO (1) for the preparation of polyMeOZO macromer (2). AAS was obtained by the lithium amide catalyzed addition of N-methylethylenediamine onto divinylbenzene according to Tsuruta et al (6). AAS was a mixture of para and meta isomers in a 36 : 64 ratio, containing 2-(N-2-aminoethyl-N-methyl)aminoethylethylbenzene(AEEB) as an impurity (see, experimental section).



A mixture of MeOZO (30.1 mmol) and MeOTs (6.0 mmol)([MeOZO]/[MeOTs] = 5.0) in 15 ml of $CHCl_3$ was kept at 90 °C under nitrogen in a sealed tube. After 4 hr the tube was opened at room temperature and a small portion of the reaction mixture was subjected to measurements of ^1H NMR spectroscopy and GPC analysis. The ^1H NMR spectrum of the mixture clearly shows the production of living polymers 1 (7). Based on the known fact that the MeOTs-initiated polymerization of MeOZO is a system of a rapid initiation with a slow propagation, the chain length of 1 (n value) was obtained to be n = 5.5 from the signal intensity ratio of NCH_2CH_2O in the oxazolinium ring versus other signals from MeOZO. This leads to the Mn value of 1 as 650. The GPC analysis of 1 gave Mn = 600 and Mw/Mn = 1.12.

Subsequently, the living species of 1 was terminated by adding AAS (6.0 mmol) to the reaction mixture of 1 and by keeping the mixture at room temperature for overnight. ^1H NMR spectrum of the mixture revealed the disappearance of the living species of 1 by reaction with AAS and the presence of styryl as well as tosylate groups to give polyMeOZO macromer 2. The GPC analysis of 2 showed a single peak and gave Mn = 750 as well as Mw/Mn = 1.15. These data indicate that the equimolar reaction of 1 with AAS produces macromer 2 containing the products of AEEB, quantitatively.

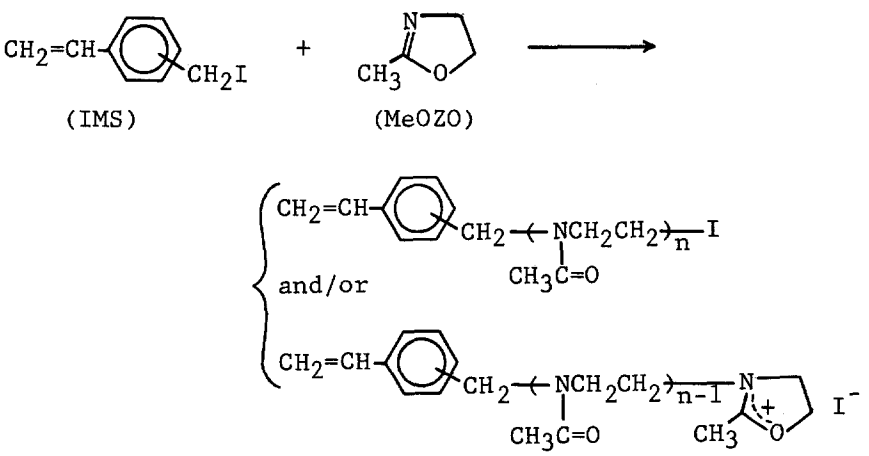
A longer chain homologue of 2 has also been prepared. A mixture of MeOZO (39.0 mmol) and MeOTs (1.9 mmol)([MeOZO]/[MeOTs] = 20.5) in $CHCl_3$ (20 ml) was kept at 90 °C for 16 hr under nitrogen. ^1H NMR spectrum of the reaction mixture revealed the production of living polymer 1 having the unit ratio [MeOZO]/[MeOTs] = 19.0 (Mn = 1800). The GPC analysis showed Mn

= 1900 and Mw/Mn = 1.29. Then, the next reaction was carried out by adding AAS (1.9 mmol) to the reaction mixture, which was kept at room temperature for overnight. The GPC measurement of product macromer 2 showed a single peak and gave Mn = 2300 and Mw/Mn = 1.26, indicating the quantitative production of macromer 2 from 1.

Thus, the two-step reaction of terminator method can be performed in one-pot and produces macromer 2 quantitatively. However, an attempt to isolate 2 of salt type or to isolate 2 of free amine type after treating 2 with an anion exchange resin has not been successful so far, because 2 or free 2 became partly insoluble during isolation procedures. Instead, the solution of 2 can be used for further reactions of 2, e.g., a free radical copolymerization.

Initiator Method

The initiator employed is iodomethylstyrene(IMS)(a mixture of para and meta isomers in a ratio of 37% : 63%). IMS was prepared by the reaction of chloromethylstyrene with NaI in acetone (8). The cationic ring-opening polymerization of MeOZO with IMS is given by the following reaction giving rise to polyMeOZO macromer (3).



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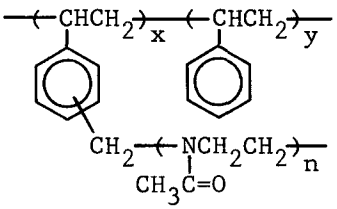
A mixture of 32.3 mmol of MeOZO and 6.8 mmol of IMS ([MeOZO]/[IMS] = 4.8) in 10 ml of N,N-dimethylformamide(DMF) was kept under nitrogen at 90 °C for 2 hr. The reaction mixture was poured into a large amount of diethyl ether to precipitate polymeric materials, which was separated and dried in vacuo giving rise to 4.41 g of a pale yellow powdery material 3 quantitatively. The structure of the polymer was determined by IR and ^{1}H NMR spectroscopy as well as elemental analysis. The IR spectrum showed a strong band at 1640 cm^{-1} due to >NC=O. The ^{1}H NMR spectrum of the polymer clearly indicates the structure of 3 having a styryl group as well as an oxazolinium iodide group at the end (7). The oxazolinium group shows a characteristic triplet-like signal centered at δ 5.1 due to OCH_2 of the ring. The MeI-initiated polymerization of MeOZO has been characterized by a rapid initiation and a slow propagation (7). IMS should be more reactive than MeI as initiator. Consequently, the chain-length of 3 was calculated from the signal integrals of methyl protons from MeOZO and phenyl protons of IMS, leading to n value in 3 as 5.3 (Mn = 700). Anal. Found: C, 50.19; H, 6.70; N, 10.57. This analytical result gives the unit ratio [MeOZO]/

[IMS] = 5.86, leading to Mn = 740. These two Mn values are very close to each other. The GPC analysis of 3 showed a single peak and gave Mw/Mn = 1.16.

Similarly, a longer chain macromer 3 has been prepared. A mixture of MeOZO (37.3 mmol) and IMS (1.8 mmol) ([MeOZO]/[IMS] = 20.7) in DMF (10 ml) was allowed to react at 90 °C for 4 hr. After usual work-up procedures a pale yellow powdery material of 3 was obtained quantitatively. The ^{1}H NMR analysis of the polymer from the integral ratio of methyl and phenyl protons gave n = 20.7 (Mn = 2000). Anal. Found: C, 50.71; H, 7.76; N, 13.33. This analytical result leads to the unit ratio [MeOZO]/[IMS] = 20.4 (Mn = 1980). These two Mn values are almost identical. The Mw/Mn value determined by GPC was 1.20, indicating a fairly narrow molecular weight distribution.

It is to be cited here that Tomalia and Zubrisky first claimed the above method to use a vinylbenzyl halide as initiator in developing polyamide materials from 2-oxazolines or 1,3-oxazines for complexing phenols and for coating materials (9).

The above two methods provide a general way to prepare macromers which are convenient starting materials for the synthesis of graft copolymers. Previously, we prepared graft copolymer 4 (10). And, very recently graft copolymer 5 has been synthesized by terminating the living propagating



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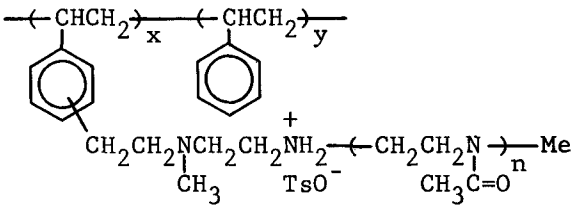

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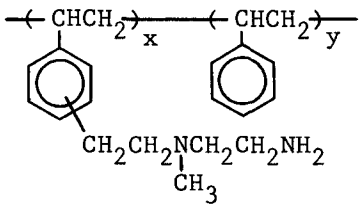
species of 1 with an AAS/styrene copolymer 6 and 5 showed enhanced antithrombogenic properties (11). Macromers 2 and 3 actually copolymerized



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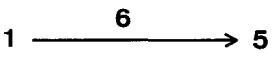

with styrene, and therefore, they provide an alternative route to graft copolymers 4 and 5, respectively. When AAS containing AEEB was copolymerized with styrene and graft copolymer 6 was isolated by usual work-up procedures, AEEB was completely removed from 6. The same is for macromer 2 containing the products of AEEB with 1. Graft copolymer 5 thus obtained did not contain the products. More detailed studies on macromers 2 and 3

prepared from pure para or meta isomers of divinylbenzene and IMS, respectively, and their applications are currently under progress in our laboratories.

EXPERIMENTAL

Materials

Solvents, $CHCl_3$ and DMF, and 2-methyl-2-oxazoline(MeOZO) were purified in an ordinary manner. Iodomethylstyrene(IMS) was prepared by the halogen exchange reaction of chloromethylstyrene with dry NaI in dry acetone (8), in which a commercial reagent of chloromethylstyrene contained para and meta isomers in 37% and 63%, respectively. The product IMS was purified by recrystallization from n-hexane at ca. -20 °C and the crystallized, pale-yellow solid was separated, dried and used as an initiator.

2-(N-2-Aminoethyl-N-methyl)aminoethylstyrene(AAS) was prepared by the lithium amide catalyzed reaction of N-methylethylenediamine with divinylbenzene (6). A commercial reagent of divinylbenzene is a mixture of diethylbenzene, ethylvinylbenzene, para- and meta-divinylbenzene in a ratio of 3.8 : 41.4 : 14.9 : 39.9(%) determined by GLC analysis for a distilled sample. The mixture was subjected to the addition of N-methylethylenediamine and distilled, bp 98 - 101 °C/0.15 Torr (lit(6) 107 °C/0.3 Torr for p-AAS). The GLC analysis of the distillate revealed the mixture ratio of p-AAS, m-AAS and 2-(N-2-aminoethyl-N-methyl)aminoethylethylbenzene(AEEB) in 27.5 : 49.4 : 23.1(%), which was used for reactions.

Measurements

^1H NMR spectra were recorded on a HITACHI R-20B(60 MHz) NMR spectrometer. IR spectra were taken on a HITACHI 260-50 IR spectrophotometer. Molecular weight data were obtained by using JASCO TRI ROTAR liquid chromatograph with a Shodex GPC-A-803 column. An eluent solvent was chloroform. The GLC analysis was carried out by a SHIMADZU GC-6A gas chromatograph with a column packed with Silicon DC-550 using helium as gas phase.

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Accepted May 2, 1985