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Synthesis of polyisoprene-poly(methyl methacrylate) block copolymers by using polyisoprene as a macro-iniferter

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Summary

Polyisoprene (PI) was pre-polymerized by using benzyl diethyldithiocarbamate (BDC) as an iniferter. The obtained PI was subsequently used to react with methyl methacrylate (MMA) in order to investigate whether the relevant block copolymers can be achieved. Results from ^{1}H-NMR and GPC reveal that the PI-PMMA block copolymers were formed. This suggests that polymerization of isoprene through the use of BDC proceeded via a (psuedo) "living" mechanism.

Introduction

The living polymerization is basically a polymerization mechanism in which propagating chains are free from terminations and/or chain transfer reactions. As a result, block copolymers and/or a homopolymer with a very low polydispersity (~1) can be obtained. Conventionally, this living mechanism was achieved by using anionic polymerization, cationic polymerization and group transfer polymerization. However, these techniques tend to be limitted in their industrial applications due to vigorous and demanding reaction conditions. Therefore, newer (and also easier to perform) synthetic routes to prepare block copolymers have been interested. These include a living radical polymerization through the use of iniferters. Otsu et al. (1-3) claimed that polymerizations of styrene and (meth)acrylate, using tetraethyl thiuramdisulfide (TD) and/or benzyl diethyldithiocarbamate (BDC) as iniferters, proceeded via the living mechanism. This was supported by obtaining PS-PMMA block copolymers. However, polydispersities of synthesized polymers were considerably high (~ 1.7-4). This is due to the fact that a bimolecular termination is not totally prevented. Therefore, this technique is considered to be a non-truly living mechanism. Nevertheless, for some applications where the level of polydispersity is not crucial, it is a good technique that can be used to prepare block copolymers (4).

This research concerns the controlled polymerization of isoprene through the use of an iniferter. Our early work (5) had shown that isoprene can be polymerized by using BDC as an iniferter. The synthesized polyisoprene (PI) was mainly in the 1,4-isomeric structure with the glass transition temperature very close to that of the trans-1, 4 polyisoprene (-50 °C).

In this paper, polymerization of methyl methacrylate (MMA) through the use of the synthesized polyisoprene is reported. The aim of this work is to investigate whether the polyisoprene can serve as a macro-iniferter, leading to the formation of PI-PMMA block copolymers.

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Experimental

Isoprene (purum grade from Fluka) and methyl methacrylate (commercial grade from Siam Fine Chemical Co. Ltd.) were purified by an ordinary method (6) prior to utilization. Toluene (analytical grade from JT-Baker) and methanol (commercial grade from Siam Beta Group Company Ltd) were used as received. Benzyl N,N-diethyldithiocarbamate (BDC) iniferter was synthesized from the reaction between benzyl chloride and sodium diethyl dithiocarbamate in absolute ethanol at room temperature, in accordance with Otsu's method (1). After the reaction had completed, mixture was extracted from a mixture of dichloromethane and distilled water (1:1) three times. An organic phase was collected and then dried with anhydrous sodium carbonate overnight. Finally, solvent was removed.

The first step for preparing PI-PMMA block copolymer is a homopolymerization of isoprene. Benzyl diethyldithiocarbamate (10.56 X 10^{-2} mol/L) was reacted with isoprene (2.8 mol/L) under UV radiation for 44 hrs. The polymerized polyisoprene was then characterized by the Gel Permeation Chromatography (GPC) technique. Measured values of number average molecular weight (Mn), weight average molecular weight (Mw), and the polydispersity of the syntheized polyisoprene were found to be 7545, 19500, and 2.6, respectively. The polyisoprene was then further used as a macro-iniferter for the block copolymerization. The macro-iniferter was used at two levels, i.e., 5.0 x 10^{-5} and 9.94 x 10^{-5} mole (number of moles were calculated based on Mn of the PI). The macro-iniferter was added to reaction flasks. Each of which contains 20 ml (4.7 mol/L) solution of MMA in toluene. Later, oxygen was removed from the mixture by nitrogen purging. The reaction tube was then sealed and exposed to ultraviolet radiation, using a Philips HPA-400 UV lamp, from a distance of 30 cm, at an ambient temperature (30 °C). After performing the polymerization for 5 hours, the product was isolated by precipitation in a large amout of methanol. Finally, the product was dried.

The percentage yield of block copolymer was determined by weighing the dried polymer. The molecular weight and polydispersity of both the polyisoprene and the block copolymers was determined by Gel Permeation Chromatography (GPC) using a Waters 150 CV apparatus equipped with the Styragel Mixed B columns and two detectors, i.e., a refractive index detector and a viscometer. The molecular weight resolving range of the columns ranges from 5 x 10^{2} to 1 X 10^{7}. Polystyrene standards were used in order to generate a universal calibration curve. Tetrahydrofuran (THF) was used as an eluent at an 1 ml/min flow rate, at 30 °C. Prior to the GPC analysis, poly(methyl methacrylate) and polyisoprene residues were removed from the block copolymer by dissolving the product in acetonitrile and cyclohexane, respectively. This was to ensure that the averaged molecular weight and polydispersity obtained from the GPC analysis was accurate. A ^{1}H-NMR spectrum were recorded by a Bruker (Advance DPX 400) spectrometer operating at 400 MHz. The polymer solution was prepared by dissolving ca. 50 mg polymer in about 3 ml. of deuterated chloroform ($CDCl_3$).

Results and discussion

Figure 1 shows a ^{1}H-NMR spectrum of the synthesized product. A small peak at 5.13 ppm corresponding to the proton at C=C in 1,4-polyisoprene can be observed. In addition, a peak at 3.59 corresponding to the proton at O-CH_3 in PMMA is also clearly seen. However, proton peaks range between 1.5 and 2.5 ppm cannot be used to differentiate PMMA from PI due to an overlap between the proton peaks of CH_2 and CH_3 in the polyisoprene and the proton peak of CH_2 in PMMA.

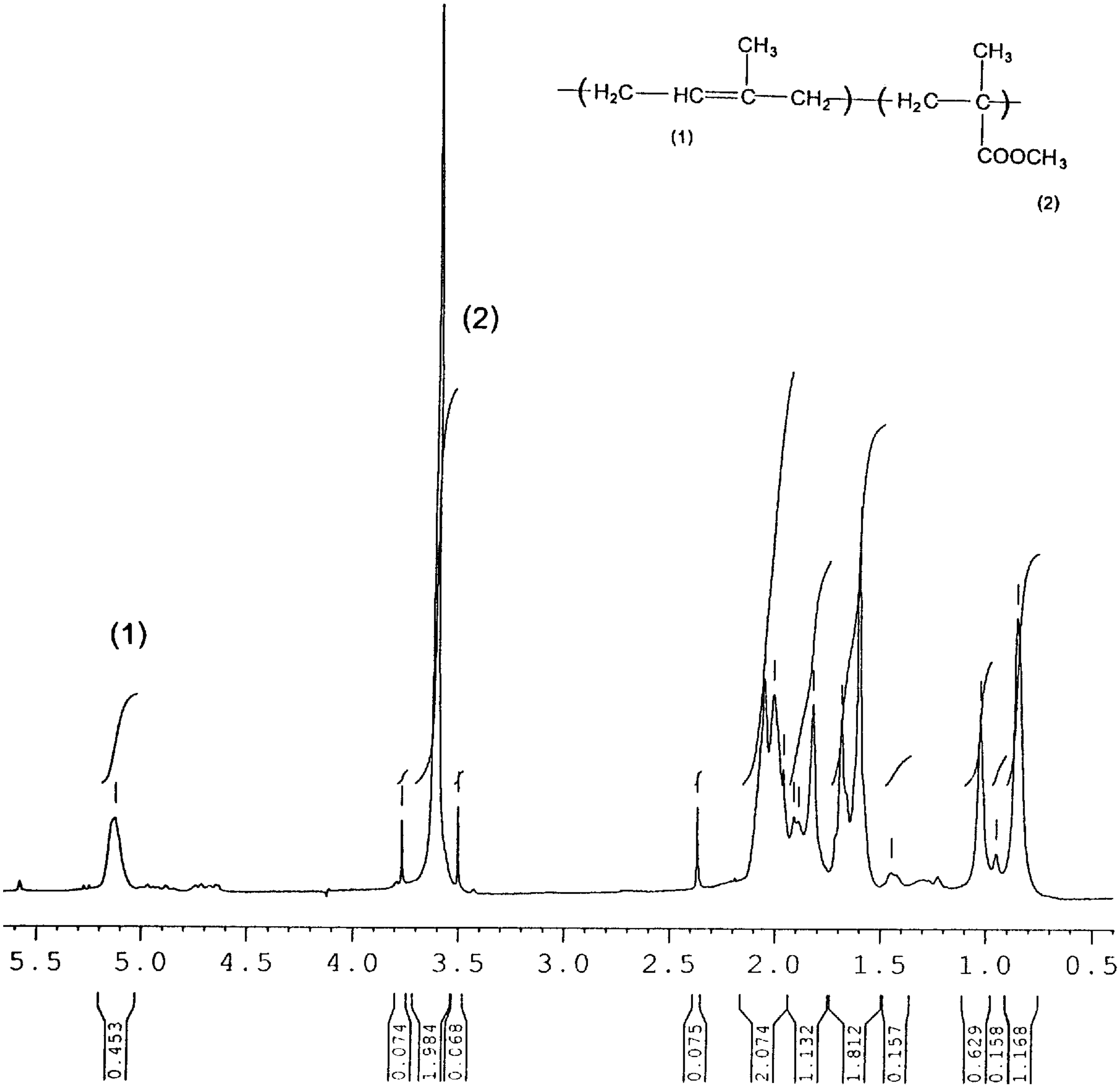

Fig. 1. ^{1}H-NMR spectrum of PI-PMMA block copolymer

The ^{1}H-NMR spectrum can also be used to determine the composition between PI and PMMA in the product. This was done by comparing the proton peak in PI (HRC=CRH) to the proton peak in PMMA (OCH_3). The composition of the product was evaluated through the integrations of the two peaks. Percentages of PI and PMMA were calculated as follows:

$$\% \text{PI} = [\,(A) / (A + B/3)]\ \text{x}\ 100$$

$$\% \text{PMMA} = [\,(B/3) / (A + B/3)]\ \text{x}\ 100$$

Where A is the area under the peak at 5.13 ppm and B is the area under the peak at 3.6 ppm. From the calculation, it was found that that percentage of isoprene in the product is 18.6%. The detail of the ^{1}H-NMR spectrum indicates that the synthesized product is some kind of a mixture between PI and PMMA. It is, however, still ambiguous whether the mixture are actually block copolymers or PI blended with PMMA. In order to clarify this, a control experiment in which the MMA was irradiated in the absence of the PI macro-iniferter has to be considered. It can be seen from the Table 1 that MMA can undergo a self-polymerization. This is evidenced by a considerably high yield (7.5 %) of PMMA. However, the yield is lower than that of PMMA polymerized in the presence of PI macro-iniferter, i.e., ~ 32.6 and 58.3 %. This result indicates that block copolymerization of MMA with PI macro-iniferter is possible. Nevertheless, the product obtained was not pure but contains some (self-polymerized) PMMA.

Table 1 . Synthesis of PI (macro-iniferter) and PI-PMMA block copolymers.

Polymerizations	Yield (%)	Mn (g/mol)	Mw (g/mol)	PDI
Isoprene (0.1 mol) + BDC (3.2×10^{-3} mol)	24.7	7545	19500	2.6
MMA (0.1 mol) + PI (5.0×10^{-5} mol)	32.6	55897	96810	1.7
MMA (0.1 mol) + PI (9.9×10^{-5} mol)	58.3	51392	95217	1.8
Control experiment (MMA (0.1 mol) without macro iniferter)	7.5	180199	434032	2.4

The crude products were purified, prior to the GPC analysis, by dissolving in the suitable selective solvents (acetonitrile and cyclohexane) in order to remove some contaminants (homopolymers). Table 1 shows molecular weights and polydispersity of products obtained from the reactions of MMA with pre-polymerized polyisoprene. Two levels of PI were used for a comparison. It was found that the more the PI used the more the product yield obtained at the expense of the molecular weight of the products. This trend is not unexpected since the iniferter can also function as an initiator. Therefore, change in the polymerization rate and/or molecular weight with respect to the initiator concentration could be similar to that from a normal free radical polymerization (7). However, a consideration of GPC traces of the two synthesized copolymers and that of the polyisoprene macro-iniferter (Figure 2) suggests that the psuedo "living" mechanism had proceeded as shown by obtaining GPC traces of the copolymers at a relatively low retention time.

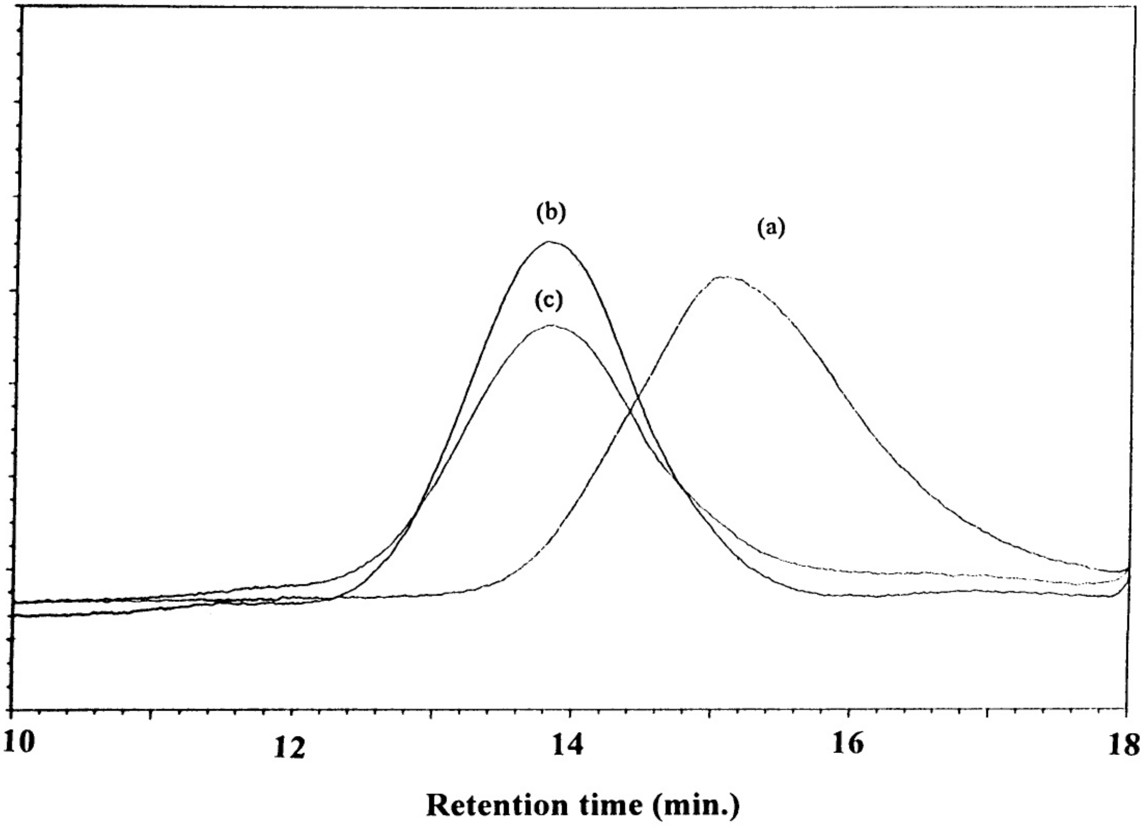

Fig.2. Overlaid GPC traces of polyisoprene macro-iniferter (a) and the two corresponding PI-PMMA block copolymers (b) and (c) .

Molecular weight of the polyisoprene increased after an addition of MMA. This indicats that the propagating chains of PI remain active. In addition, the GPC traces were found to be monomodal (single trace) and not bimodal as might be expected for a mixture of two polymers. It should be noted from the Table 1 that the molecular weight (Mw) of PMMA block is about 5 times larger than that of the PI block (95217/19500 and/or 96810/19500). Therefore, a single GPC trace may be unlikely if the product was a blend of PI and PMMA. Furthermore, the distribution curves of the two block copolymers are narrower than that of the PI. This can be interpreted that the polydispersity of the products are lowered (see also Table 1). This phenomenon is unlikely if PMMA obtaining from a self-polymerization of MMA was a majority of the product.

Finally, it worth mentioning that the possibility in obtaining PI-PMMA random copolymer from the reaction between PI macroiniferter and MMA is unlikely. This is due to the fact that the isoprene and MMA were applied to the reaction sequentially and not concurrently. In addition, the obtained PI was purified prior to the block copolymerization in the second step. Therefore, isoprene residue was removed. Nevertheless, a Differential Scanning Calorimetry (DSC) and/or Transmission Electron Microscopy (TEM) may be used to differentiate between block- and random copolymer. Attempt in examining micro-phase separation in the block copolymers has yet to be determined. Further study is strongly expected for clarifying this in the future.

Conclusion

On a basis of the results from ^{1}H-NMR, GPC and a control experiment, it can be concluded that PI-PMMA block copolymers were prepared. This suggested that polyisoprene, pre-polymerized with BDC, can serve as a macroiniferter.

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References

1. Otsu T, Yoshida M, Kuriyama A (1982) Polym. Bull. 7: 45
2. Otsu T, Tazaki T (1986) Polym. Bull. 16: 277
3. Otsu T, Matsunaga T, Kuriyama A, Yoshioka M (1989) Eur. Polym. J. 25: 643
4. Wootthikanokkhan J, Chaplin RP, Burford RP (1996).J. Appli. Polym. Sci. 62: 835
5. Kongkaew A, Wootthikanokkhan J (1999) ScienceAsia, 25: 35
6. Braun D, (1984) Practical Macromolecular Organic Chemistry. (3 rd edition), Harwood Academic Publishers Germany
7. Stevens MP (1990) Polymer Chemistry. 2nd Edn, Oxford University Press, New York (p.203)