RESEARCH ARTICLE

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Polymerization of Isoprene by Using Benzyl Diethyldithiocarbamate as an Iniferter

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ABSTRACT The polymerization of isoprene through the use of benzyl N,N-diethyldithiocarbamate (BDC) as an iniferter was investigated. The monomer concentration used was kept constant at 2.8 mol/L while the BDC concentration was varied. The polymer product was characterized by Fourier Transform Infrared Spectroscopy (FTIR), Proton Magnetic Resonance (^{1}H-NMR), and Differential Scanning Calorimetry (DSC) and the results showed that the product was mainly 1,4-polyisoprene. The molecular weight, polydispersity, and percentage yield of the polyisoprene obtained were affected by the BDC concentration. The percentage yield did not increase linearly with the BDC concentration but increased initially and then decreased after a critical BDC concentration was reached. The molecular weight of the polyisoprene decreased with BDC concentration. The polydispersity ranged between 1.8 and 4.7 and decreased with increasing BDC concentration.

KEYWORDS: iniferters, polyisoprene, living radical polymerization.

INTRODUCTION

New synthetic routes for preparing well-defined polymers from vinyl monomers are of considerable interest.[1] Conventinoal techniques such as living anionic polymerization and Group Transfer Polymerization (GTP) have tended to be limited in their industrial applications due to their vigorous and demanding reaction conditions. For example, the preparation of a poly(methyl methacrylate)-poly(butyl acrylate) block copolymer has to be carried out at a reaction temperature of -78°C.[2] Moreover, the monomer and solvent have to be carefully purified. As a result of these stringent requirements, it is desirable that a new technique of polymerization which is relatively simple and potentially applicable to industry be developed. This includes living radical polymerization. Normally, a radical polymerization cannot be used to achieve well-defined polymers such as block copolymers and/or polymers with low polydispersities. However, if the reactions are controlled so that the propagating chains are free from bimolecular terminations and chain transfer reactions, a "living" radical polymerization can be approached. The strategy to achieve such conditions is to find a capping agent that reversibly reacts with the propagating chains. In the presence of capping agents, the propagating chains are temporarily blocked and prevented from undergoing chain transfer and termination reaction. Capping agents are, for example, tetraethylthiuram disulfide (TD), benzyl N,N-diethyldithiocarbamate (BDC), and p-xylylene bis(N,N-diethyldithiocarbamate) (XDC), these being organic sulfur compounds with low decomposition energies (Fig 1). These compounds are called "iniferters" (<u>ini</u>tator - chain trans<u>fer</u> agent - <u>ter</u>minator).

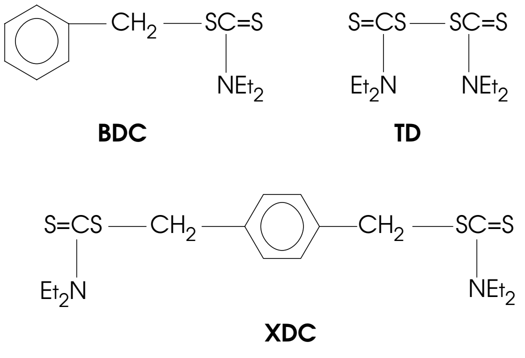


Fig 1. Chemical structures of some iniferters.

Under suitable conditions, the iniferter compound (designated as **A–B** in Fig 2) splits (through S-S or C-S bonds) into two radicals, these being a reactive radical **A•** (which participates only an initiation) and a non-reactive radical **B•** (which cannot enter initiation but acts as a primary radical terminator). The formation of macro-radicals can be

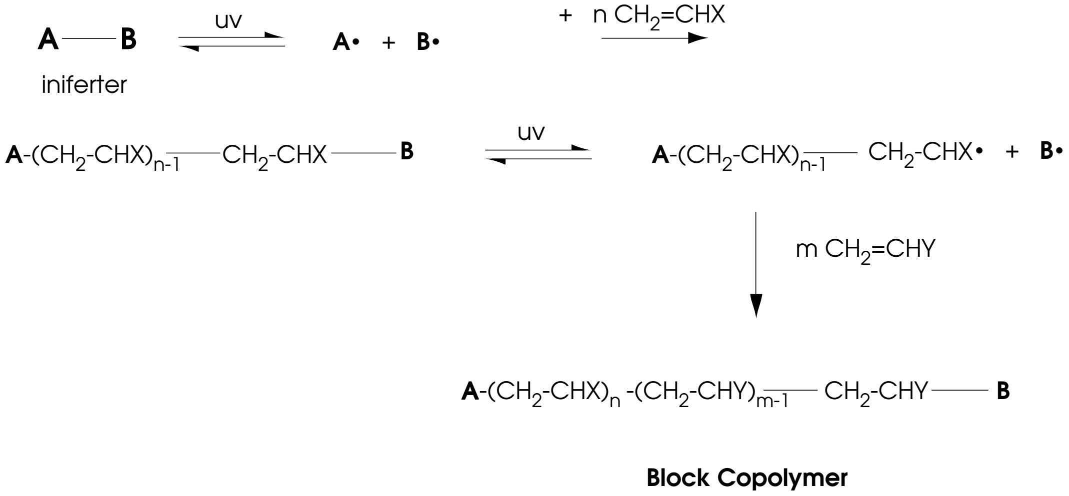


Fig 2. Basic mechanism for the living radical polymerization of vinyl monomers with an iniferter.

stopped by terminating the condition, and the polymer chains can be isolated by being precipitated in a suitable non-solvent. The polymers obtained are macro-iniferters and can be used for further polymerization with other monomers to form block copolymers. According to Otsu *et al,*[3] the reaction mechanism is simply considered as an insertion of monomer in between C-S bond in the iniferter shown in the following equations (Fig 2).

Otsu *et al*[3-5] have shown that polymerizations of styrene and/or methyl methacrylate through the use of the BDC iniferter have proceeded through a "living" mechanism. This was confirmed by obtaining low polydispersities of the polymers produced, the polydispersities ranging between 1.7 and 3.4. In addition, the percentage monomer conversion increased with increasing molecular weight, indicating that the monomers reacted at the end of the propagating chains. It was also found that the reaction could lead to a block copolymer formation, if the second monomer was added to the homopolymer from the first step.[5] For relatively strong electron-deficient monomers such as butyl acrylate and methyl acrylate, the polymerization by using BDC will not occur. However, Otsu *et al*[6] have found that these monomers can be polymerized successfully via a living mechanism by using a two-component iniferter, *ie*, BDC in combination with TD. In addition, iniferters can be used to prepare telechelic polymers. For example, polystyrene with carboxylic groups at both chain ends have been prepared by Otsu *et al.*[7] using a two-component iniferter system (4,4'-azobiscyanovaleic acid and dithiodiglycol acid). The resulting telechelic polystyrene can undergo polycondensation with polyethyleneglycol, leading to a block copolymer.

This research work concerned the polymerization of isoprene through the use of BDC. The aim was to investigate the effects of the BDC concentration upon percentage yield, molecular weight, and polydispersity of the polymerized polymer.

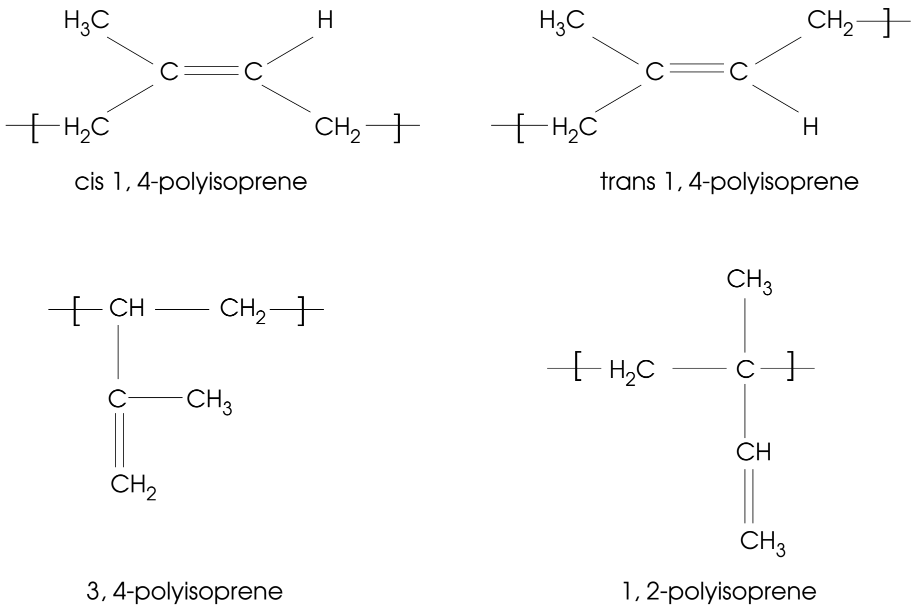
MATERIALS AND METHODS

Monomer, solvents and iniferter preparation

The isoprene used was a purum grade supplied by Fluka. The monomer was purified prior to use by an ordinary method.[8] Toluene used as a solvent in this work was an analytical grade from the JT-Baker, and a commercial grade of methanol was used as a non-solvent for precipitation of the product and supplied by the Siam Beta Group Company Ltd. All the solvents were used as received. Benzyl N, N-diethyldithiocarbamate (BDC) iniferter was synthesized from a reaction between benzyl chloride and sodium diethyldithiocarbamate in absolute ethanol at room temperature. After the reaction was completed, the mixture was extracted with a mixture of dichloromethane and distilled water (with the ratio of 1:1) three times. The organic phase was collected and dried with anhydrous sodium carbonate overnight, and dichloromethane was easily removed at 40°C.

Polymerization procedures

The polymerization was undertaken at a fixed isoprene concentration (2.8 mol/L) while the BDC concentration was varied. The required amount of isoprene was mixed with the BDC iniferter and toluene solvent in a reaction flask. After that, oxygen



cis 1, 4-polyisoprene

trans 1, 4-polyisoprene

3, 4-polyisoprene

1, 2-polyisoprene

Fig 3. Chemical structures of polyisoprene.

was removed from the mixture by nitrogen-purging. The reaction tube was 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 the polymerization finished (the reaction times used were 22 and 44 hrs.), the product was isolated by being precipitated in a large amout of methanol and dried.

Characterization

The percentage conversion of the isoprene was determined by weighing the dried polymer. The molecular weight and polydispersity of the polymer were determined by Gel Permeation Chromatography (GPC) using a Waters 150 CV apparatus equipped with the Styragel Mixed B columns and two detectors, *ie*, a refractive index detector and a viscometer. The molecular weight resolving range of the columns is betweeen 5×10^2 and 1×10^7. 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.

Fourier Transform Infrared Spectroscopy (FTIR) spectrum of the polymerized polyisoprene was obtained by using a Bruker (VECTOR 33) spectrophotometer. The polymer was casted onto a ZnSe window cell, and the spectrum was recorded.

A ^{1}H-NMR spectrum was recorded by a Bruker (Advance DPX 400) spectrometer operating at 400 MHz. The polymer solution was prepared by dissolving ca 50 mg polymer in 3 ml of deuterated chloroform ($CDCl_3$).

The thermal characteristic of the polymerized polymer was analysed by Differential Scanning Calorimetry (DSC). The analysis was performed using a Perkin Elmer (Series 7) instrument. The heating rate was 10°C/min, and the temperature range was from -100 to 100°C.

RESULTS AND DISCUSSION

Characterization of the synthesized polyisoprene

The homopolymerization of isoprene can take place with a cis-1,4, trans-1,4, 3,4, or 1,2 connection (Fig 3). The type of isomeric structure influences properties of the polyisoprene.[9] For example, the trans 1,4- polyisoprene has a higher degree of crystallinity and glass transition temperature than the cis 1,4-polyisoprene. Therefore, it is important to characterize the chemical structure of the product. In this work, this was undertaken by using various techniques, including FTIR, ^{1}H-NMR, and DSC.

Fig 4 shows the FTIR spectrum of polyisoprene polymerized with BDC at the iniferter concentration of 10.56×10^{-2} mole/L. The spectrum is interpreted and summarized in Table 1.

It can be seen that the spectrum shows characteristic absorption bands of significant chemical bonds in both 1,4-polyisoprene and 3,4-polyisoprene. However, detail of this FTIR spectrum was insufficient to give a ratio of the microstructure

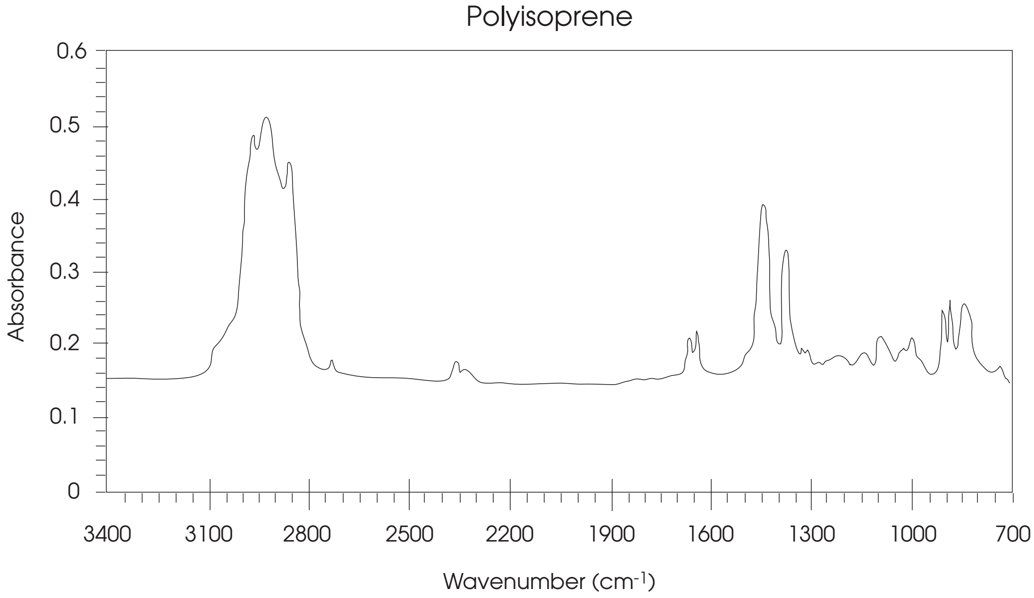


Fig 4. The FTIR spectrum of the polyisoprene.

between 1,4- and 3,4- isomeric structure. In order to determine the ratio, the ^{1}H-NMR spectrum shown in Fig 5 was used. The characteristic peaks are also summarized in Table 2. The percentages of 1,4- and 3,4-polyisoprenes were estimated using the peak area ratio of the areas under the peaks at 5.13 and 4.70 ppm, respectively, the calculation being based on the following equations.

$$\% \text{ 1,4-Polyisoprene} = [\, 2m / (2m + n)\,] \times 100$$

$$\% \text{ 3,4-Polyisoprene} = [n / (2m + n)] \times 100$$

where

m = The integrated area of the methine proton adjacent to C=C of 1,4-polyisoprene at $\delta = 5.13$

n = The integrated area of the methylene protons adjacent to C=C of 3,4-polyisoprene at $\delta = 4.70$

Table 1. The specific IR absorption peaks of the polymerized polyisoprene

Wavenumber, (cm^{-1})	Corresponding Chemical Bond
1666	$C{=}C_{\text{1,4-PI}}$ (ν)
1645	$C{=}C_{\text{3,4-PI}}$ (ν)
1450	CH_2 (δ_S)
1376	CH_3 (δ_S)
889	$=C{-}H_{\text{3,4-PI}}$ (δ)
837	$=C{-}H_{\text{1,4-PI}}$ (δ)

Table 2. The specific ^{1}H-NMR peaks of the polymerized polyisoprene.

Chemical Shift (ppm)	Corresponding Proton Type
5.13	1H at C=C of 1,4-PI
4.70	2H at C=C of 3,4-PI
1.5-2.5	5H of CH_3 and CH_2 in 3,4-PI 7H of CH_3 and CH_2 in 1,4-PI

In Fig 5, it can be seen that the integrated peak areas at 4.70 and 5.13 ppm were 0.684 and 6.023, respectively. These results indicated that the majority of the polyisoprene product was 1,4 isomeric structure (94.6%)

Fig 6 shows the DSC thermogram of the polymer. It can be seen that the DSC thermogram shows an endothermic transition temperature of -48°C. This temperature was higher than the glass transition temperature of cis-1,4-polyisoprene, which is -73° C,[10] but close to the glass transition temperature of trans-1,4-polyisoprene -53°C.[10] Normally, the glass transition temperature of cis-1,4-polyisoprene is lower than that of trans-1,4-polyisoprene due to the fact that the lower the cis content, the less amount the crystallinity that the polymer can develop.[9] In relation to this work, the DSC thermogram in Figure 6 suggested that the product may probably be trans 1,4-polyisoprene. However, in order to clarify this the ^{13}C-NMR spectrum should be considered and used to differentiate between cis- and trans-1,4 polyisoprene. In addition, a slight increase in the glass transition temperature of the polymerized

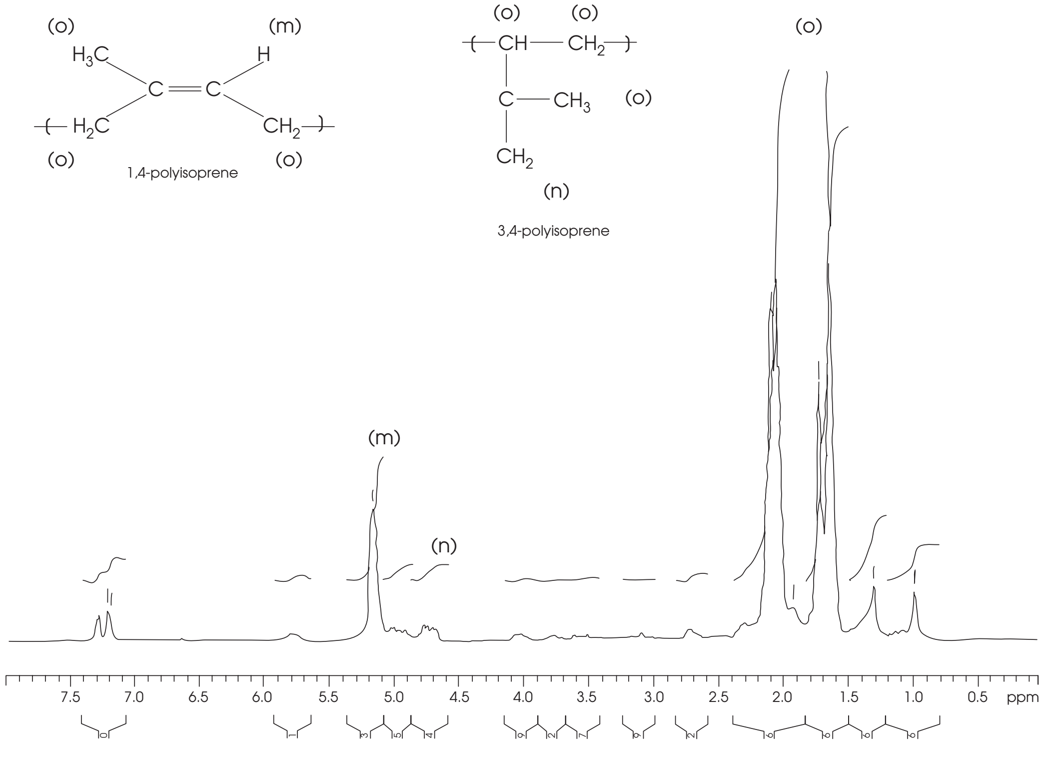


Fig 5. The ^{1}H-NMR spectrum of the polyisoprene.

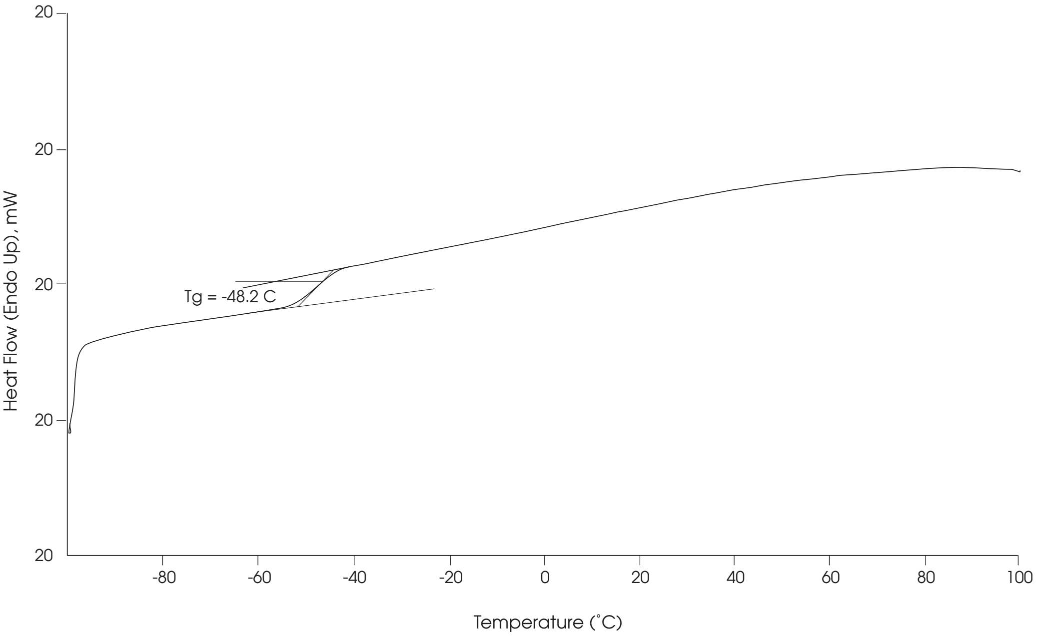


Fig 6. The DSC thermogram of the polymerized polyisoprene.

polyisoprene as compared to trans-1,4 polyisoprene may be attributed to the presence of 3,4-polyisoprene. Normally, the more the 3,4- isomeric content, the higher the glass transition temperature of the polyisoprene. Work by Halasa[11] showed that polyisoprene containing 62% of 1,4-, 37% of 3,4-, and 1% of 1,2-isomeric structure had a Tg of -39°C while polyisoprene containing 30% of 1,4-, 63% of 3.4- and 7% of 1,2-isomeric structure had Tg of -7°C. The relatively high glass transition temperature of 3,4-polyisoprene may be attributed to the presence of bulky side groups (-C(CH_3)=CH_2) which increase energy barrier to rotation and thus restrict the segmental motions of the polymer chains.[12]

Effect of BDC concentration

Fig 7 shows the effects of the BDC concentration on percentage conversion of isoprene and molecular weight of the polyisoprene. It can be seen that the conversion did not increase linearly with increasing BDC concentration. The conversion initially increased as the BDC concentration was increased from 2.64 x 10^{-2} to 10.56 x 10^{-2} mol/L and tended to decrease as the BDC concentration was increased from 10.56 x 10^{-2} to 15.84 x 10^{-2} mol/L. The reasons for this include the concept of a critical value of iniferter to monomer mole ratio. Acccording to Reghunadhan Nair[13] there was a critical inifeter concentration (at a fixed monomer comcentration) at which the maximum percentage conversion of monomers such as styrene and MMA had reached. It was explained that this was related to the characteristic of the iniferter. In other words, the iniferter can generate both initiators (benzyl radical) and capping agents (dithiocarbamyl radicals) upon irradiation under UV light. At a high BDC/monomer mole ratio, there were more dithiocarbamyl radicals available which would serve as capping agents. Therefore, propagating chains have less chance to undergo propagation (as well as a bimolecular termination), leading to a lower percentage conversion of the monomer.

It should also be noted that the highest percentage yield of the polyisoprene obtained in this work was approximately 25%. This is considerably low as compared to the percentage yield of polystyrene and/or poly(methyl methacrylate).[3,4] Otsu *et al*[4] showed that the polymerization of styrene through the use of BDC iniferter (7.7 x 10^{-3} mol/L) for 33 hrs. resulted in the polystyrene with the yield of approximately 38 %. These results suggested that the polymerization rate of isoprene was low as compared to that of styrene. An attempt to accelerate the polymerization rate by using higher isoprene concentration is not recommended since the higher the concentration, the more the exothermic heat of polymerization produced. The boiling point of isoprene is 33°C, so too high temperature in the reaction flask could be a technical problem, unless heat transfer from the reaction is properly provided.

Regarding the effect of the BDC concentration on the molecular weight of the polyisoprene, it can be seen from Fig 7 that the molecular weight of the polymer decreased with the BDC concentration. This was the same as expected from the conventional free radical polymerization where the kinetic chain length decreases with initiator concentration. This is due to the fact that the more BDC, the more the initiating species and the lower the kinetic chain length of the polymer.

Fig 8 shows changes in polydispersities of the polyisoprene with BDC concentration. It can be seen

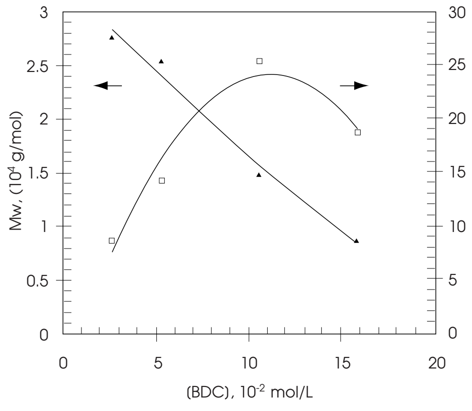


Fig 7. Plots of BDC concentration against molecular weight and percentage conversion. (44 hrs reaction time)

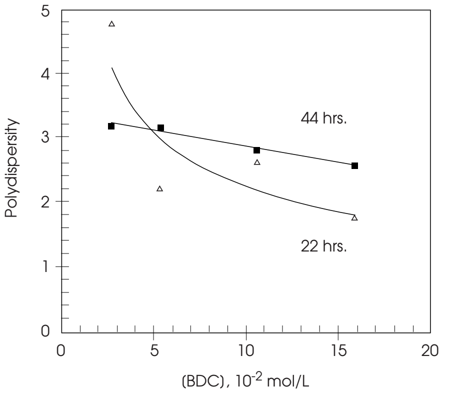


Fig 8 Change in polydispersity of the polyisoprene with BDC concentration at two different reaction times; 22 hrs (Δ) and 44 hrs (■).

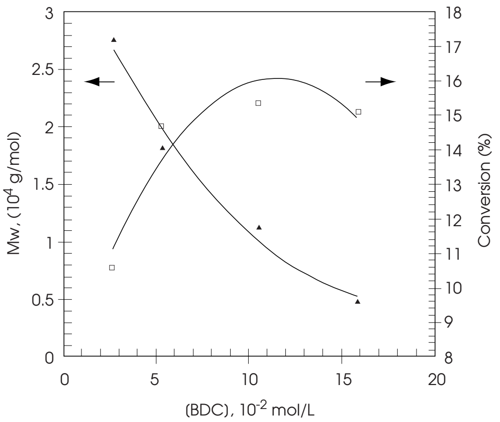


Fig 9 Plots of BDC concentration against molecular weight and percentage conversion. (22 hrs reaction time).

that the polydispersities ranged from 1.8 to 4.7 (for the reaction time of 22 hrs.) and from 2.5 to 3.2 (for the for the reaction time of 44 hrs.). In addition, the polydispersities tended to decrease with BDC concentration. This indicated that the higher the BDC concentration, the less chance the termination and/or chain transfer reactions occurred.

Fig 9 shows the relationships between the BDC concentration, the percentage conversion of isoprene, and the weight average molecular weight of polyisoprene at a polymerization time of 22 hrs. It can be seen that the trend was similar to that from Fig 7, *ie*, the molecular weight decreasing with the BDC concentration, and the conversion initially increasing and tending to decrease after the critical BDC concentration. No further attempts have been made in this paper, upon the effect of the reaction time on the chemical structure, percentage yield, and molecular weight of polymeized polyisoprene. However, it is hoped to clarify in the future work. In addtion, block copolymerizations of isoprene with styrene and methyl methacrylate are being investigated, and hopefully these upcoming experimental data will reveal whether or not the polymerization of isoprene with the BDC has proceeded *via* a "living" mechanism.

CONCLUSION

Isoprene can be polymerized by using benzyl diethyldithiocarbamate (BDC) iniferter. The majority of the polymerized polyisoprene was 1,4-isomeric structure. The concentration of benzyl diethyldithiocarbamate [BDC] significantly affected both molecular weight and percentage yield of polymerized polyisoprene. The molecular weight decreased with the BDC concentration while the percentage yield initially increased and tended to decrease after a critical value of BDC concentration had reached.

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