

Synthesis of functional polyisobutene

I. Copolymerization of isobutene with 4-vinylbenzyl N,N-diethyldithiocarbamate

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Received: 23 August 2001/Revised version: 29 October 2001/ Accepted: 2 November 2001

Summary

A special monomer 4-vinylbenzyl N,N-diethyldithiocarbamate (VBDC) was synthesized firstly, and then the cationic copolymerization of VBDC with isobutene was investigated. The results of $^1\text{H-NMR}$, EA and GPC (with UV detector) indicated that VBDC could copolymerize with isobutene and form the copolymer, and the units of VBDC incorporated into copolymer chains increased with the increasing of the feed ratio of VBDC. However, there has apparent discrepancy between the VBDC in the monomer feed and the VBDC incorporated into the copolymer chain, which is probably due to the relatively lower reactivity of VBDC. In the presence of VBDC, the MWD is narrower than that of in absence of VBDC under the similar experimental conditions. For cumyl methyl ether/ TiCl_4 initiating system, the M_w/M_n could be slightly narrowed from 1.55 (no VBDC) to 1.33 (with VBDC) in the mixed solvents of n-hexane and CH_2Cl_2 (15/10,V/V), while cumyl chloride / TiCl_4 initiating system, the M_w/M_n is narrowed from about 5.0 (no VBDC) to about 1.5 (with VBDC) with n-hexane and CH_2Cl_2 (10/10,V/V) as the mixed solvents. When benzyl N, N-diethyldithiocarbamate (BDC) was used as the model compounds instead of the VBDC, the similar results of M_w/M_n were obtained. These results demonstrated that the VBDC functions as the monomer electron donor (ED) in this polymerization system.

Introduction

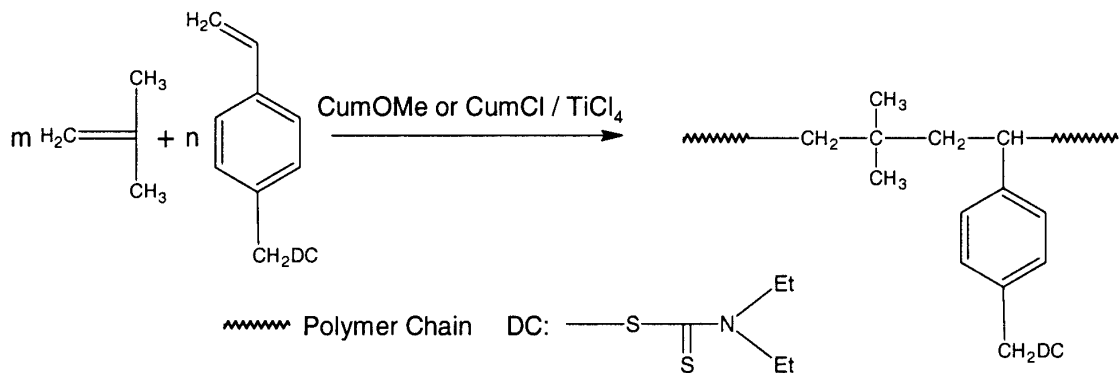
The discovery of the living carbocationic polymerization (LCP) of isobutene provided a valuable tool in the synthesis of a wide variety of novel materials with potential commercial interest. [1] These novel materials include macromonomers, techelics, polymers with pendent functional groups, star-shaped macromolecules, block and graft polymers and hyperbranched polymers. [2-4] Most of the LCP systems require external nucleophilic additives (or electron donors, EDs), such as esters, amines, amides and chelating compounds to modify or improve their livingness. Although the actual roles of these compounds have not been completely revealed yet, some interpretations on their positive effects on LCP have been reported.[5]

The living cationic polymerization of isobutene coinited by BCl_3 and TiCl_4 system yields invariably and quantitatively tertiary chlorine-terminated PIB after quenching with methanol. Depending upon the functionality of the initiator used, mono-, di-, tri-, and even tetrafunctional tert-chlorine-telechelic PIBs can be synthesized. The tert-Cl chain end is useful for further functionalizations and thus for the synthesis of unique PIBs. [6]

Puskas et al [7] had synthesized the hyperbranched PIB by copolymerization of isobutene with 4-(1-hydroxyl-1-methyl)ethyl styrene which was used as inimer. To our knowledge, synthesis of functional PIB by copolymerization of isobutene with functional monomers has scarcely been investigated.

In the early 1980s, Takayuki Otsu et al [8] found that when benzyl N,N-diethyldithiocarbamate was used as a photo-iniferter, the polymerization of vinyl monomers such as styrene and methyl methacrylate(MMA) proceeded via a living free radical mechanism. In the ensuing reports, VBDC was used as photo-iniferter monomer in radical copolymerization of styrene with MMA. [9]

Enlightened by these precursory accomplishments and combined with the research practice of our group on the cationic polymerization of isobutene, we initiate a program in our lab attempt to prepared various functional polyisobutene by copolymerization of isobutene with various functional monomers. Adopting VBDC as functional comonomer is based on the following points: (1) N,N-diethyldithiocarbamate is an electron donor and styrene is highly cationic polymerizable monomer, and therefore VBDC is reasonably expected to be a monomer ED, which would incorporate into the PIB chain via its double bond (See



Scheme 1

Scheme 1); (2) the pendent functional group N,N-diethyldithiocarbamate can be used as photo-iniferter to design the graft polymers with PIB as backbone via combining the LCP and living free radical polymerization mechanism; (3) the attached N,N-diethyldithiocarbamate functional group can provide built-in antioxidant, having also vulcanization and covulcanization ability. In the present investigation we focused only on the cationic polymerization of isobutene and VBDC.

Experimental

Materials

CH_2Cl_2 (Beijing Yili Fine Chemical Company, AR) and n-Hexane (Beijing Chemical

Factory, AR) was refluxed over CaH_2 for 24hrs, then distilled before use. TiCl_4 (Beijing Chaoyang Xihui Chemical Factory, AR), p-chloromethylstyrene (ARCOS), di-tertbutyl pyridine (Aldrich), α -methylstyrene (ACROS), benzyl chloride (Beijing Chemical Factory) and sodium N,N-diethyldithiocarbamate (Beijing Chemical Factory, AR) are used as received. Isobutene and CH_3Cl (Yanshan PetroChem Company) were used without further purification. Cumyl methyl ether (CumOMe) [10] and cumyl chloride (CumCl) [11] were synthesized and purified as described in literatures. VBDC was synthesized from the reaction of p-chloromethylstyrene with sodium N,N-diethyldithiocarbamate according to the method reported by Otsu etc [9] and characterized by $^1\text{H-NMR}$. Benzyl N,N-diethyldithiocarbamate (BDC) was synthesized and purified according to the method described by Otsu etc. [8]

Polymerizations

The polymerizations were carried out in tube-like glass reactors. The reactors were purged with dry nitrogen, then evacuated and flamed out. The operation was repeated three times. The solvents, initiator, BDC, VBDC solution and DtBP were transferred by syringes into the reactors. Then these mixtures were cooled by ethanol/liquid nitrogen bath to -80 before IB was added. Polymerizations were induced by adding a predetermined amount of TiCl_4 with a syringe. Prechilled methanol was used for quenching the polymerization. The polymer products were purified by repeatedly dissolution (petroleum ether mixed with CH_2Cl_2) and / precipitation (methanol). The conversions were determined gravimetrically.

Characterizations

$^1\text{H-NMR}$ spectra (in CDCl_3) were recorded by a VXR 300S spectrometer at room temperature. Molecular weights were determined by GPC (Waters) equipped a series Styragel columns (HT3, HT5 and HT6E), a RI detector (Waters 2410) and a UV detector (Waters 996, Photodiode Array Detector). The VBDC units in copolymers were determined by Elemental Analysis.

Results and Discussion

A The Evolution the Copolymerization of IB with VBDC

The yield-evolution of the copolymerization of VBDC with IB is shown in Figure 1 and Figure 2.. Since the cationic polymerization of isobutene, in general, proceeds too fast to take out samples for kinetic study, we conducted the polymerization experiment by use of a series of reactors. At zero time an appropriate amount of TiCl_4 coinitiator was added to five tube-like reactors charged with IB/VBDC/CumCl in dichloromethane and n-hexane solvents at -80 . After a set reaction time the polymerization was quenched by adding a few milliliters prechilled methanol. From Figure 1 it can be seen that in 5 minutes, the overall conversion is approximately up to 90%, then in about 60 minutes close to 100%.

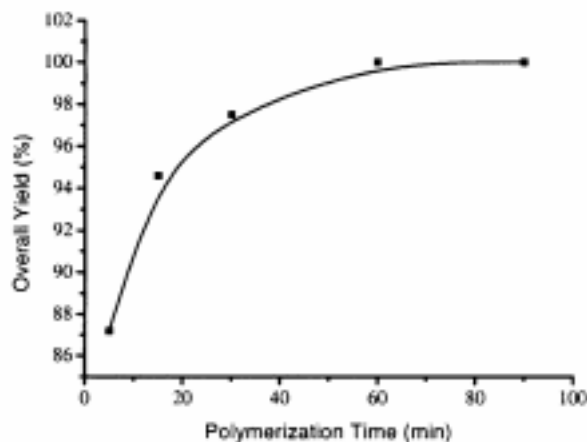


Figure 1. Overall Yields vs Polymerization Time (1) Isobutene 36.04 mmol, [VBDC] / [IB] = 2.5%(mol), CH₂Cl₂ 10ml, n-hexane 10 ml, TiCl₄ 2.25 mmol, CumCl 0.23mmol, Temperature - 80 , terminated by methanol. (2) Overall yield (weight of polymer / weight of IB and VBDC).

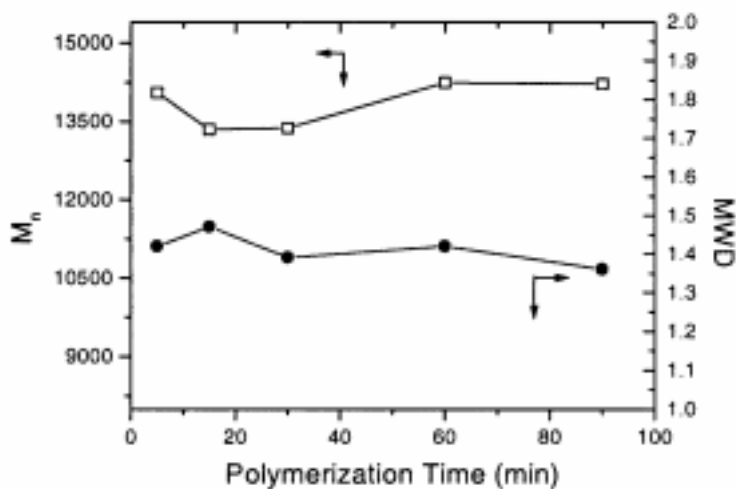


Figure 2. The Dependence of M_n and MWD upon Polymerization Time (Conditions as Fig. 1)

Figure 2 shows the dependence of M_n and MWD upon polymerization time. It is seen that the M_n keeps almost constant and the MWD decreases with polymerization time (close to 1.35).

B. Effect of [VBDC] / [IB] Ratios on Copolymerization of IB with VBDC

The copolymerization of VBDC with isobutene at different feed ratios was carried out with CumOMe/TiCl₄ as initiating system at -80 in mixed solvents. When the TiCl₄ was introduced into the reactors to start the polymerization, Runs V2-2, V2-3, V2-5 and V2-6 turned into deep red while the control one (Run V2-1) turned only into slight yellow. It was observed that in the presence of VBDC all the polymerization runs are much slower than Run V2-1 which is completed within a few seconds. Run V2-6 became heterogeneous system due to the high VBDC content which led to precipitation of the copolymer produced in the later period of polymerization. The results are listed in Table 1 and the ¹H-NMR of sample Run

V2-6 is showed in Figure 3.

Table 1 The Results of the Cationic Copolymerization of Isobutene with VBDC⁽¹⁾

Run	[VBDC]/[IB] (%,mole)	Yield % ⁽²⁾	S %wt ⁽³⁾	VBDC ⁽⁴⁾	$M_n \cdot 10^{-4}$	M_w/M_n
V2-1	0	98.2	0	0	1.69	1.55
V2-2	0.33	94.2	0.305	0.268	2.01	1.35
V2-3	0.5	93.3	0.49	0.44	1.94	1.38
V2-5	2.45	91.3	1.05	0.96	2.18	1.33
V2-6	4.9	88.0	1.535	1.43 ⁽⁵⁾	1.89	1.32

(1) Isobutene 45.63 mmol, CH₃Cl 15ml, n-hexane 10 ml, TiCl₄ 4.56 mmol, CumOMe 0.224 mmol, Temperature -80, Polymerization Time 150 min, terminated by methanol. (2) Overall yield (Weight of Polymer/ Weight of Isobutene and VBDC). (3) In copolymers, determined by Elemental Analysis. (4) VBDC incorporated into the copolymer (% , mole ratio). (5) 1.53% (mole) by ¹H-NMR.

Table 1 showed that with the increasing of the feed ratio of [VBDC]/[IB], the units of VBDC incorporated into copolymer chains also increased. There are an apparent discrepancy between the VBDC in the monomer feed and the VBDC incorporated into the copolymer chain, which is probably due to the relatively lower reactivity of VBDC. The relatively narrower MWD of sample V2-1 is due to the fact that CumOMe is the initiator and the counterion thus formed in situ can stabilize the active species. In the presence of VBDC, the M_w/M_n became slightly narrower than that without VBDC. This indicated that the VBDC may play also the role as an ED and the VBDC-TiCl₄ complexes very favorably affect the livingness of the carbocationic polymerizations, i.e. to give rise to narrower MWD (Compare to Reference [12]). In the Figure 3, the chemical shifts of δ 3.73, 4.05(q, 4H, N-CH₂), δ 4.52 (s, 2H, C₆H₄-CH₂), and δ 7.33 (m, 4H, C₆H₄) can be seen, but δ 5.80, 5.58, 5.28, 5.13 (q, 2H, =CH₂), and δ 6.86, 6.73, 6.64 6.51 (q, 1H, =CH-) which are corresponding to the vinyl group disappeared. (Assignment of the chemical shifts, see reference [13]).

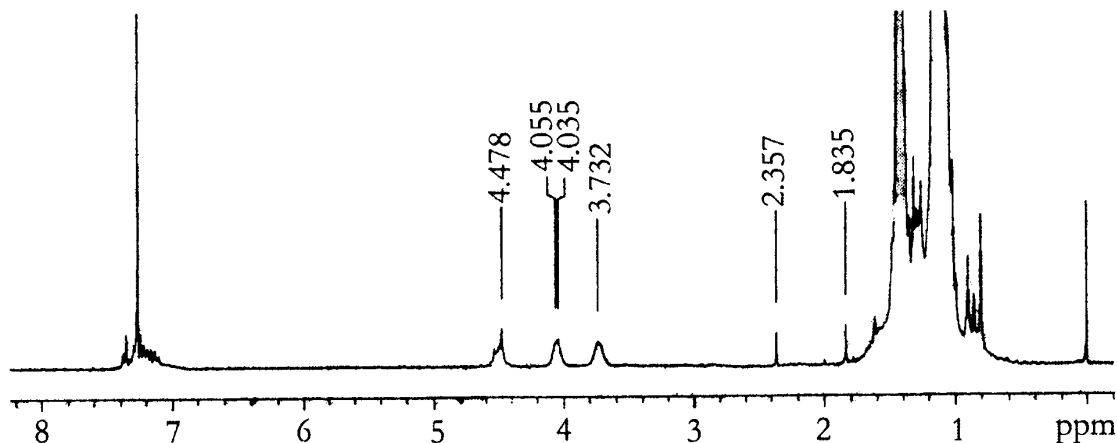


Figure 3. The ¹H-NMR (300MHz) of the Copolymer of IB with VBDC (Run V2-6, in CD₃Cl)

In Figure 4, the GPC traces of some typical samples of the copolymers of VBDC with IB recorded by UV and RI detectors are compared. As it is shown that the UV absorption at 282nm assigned to the DC functional group (See reference[8]) was absent for sample Run V2-1, while for all other samples from V2-2 through V2-6 the absorption at 282nm is observed clearly. The similar results are shown by RI traces. These results illustrated that all samples except Run V2-1 are copolymers from VBDC and IB.

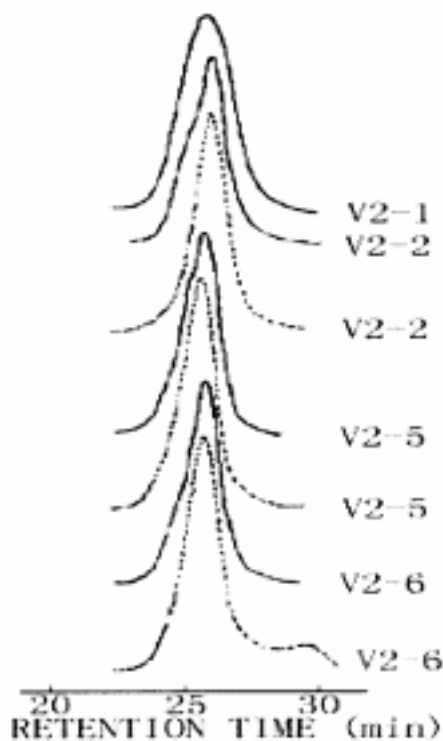


Figure 4. The GPC Traces of Some Typical Samples (Data in Table 1. V2-1 no absorption at 282nm, RI: solid line, UV: dotted line)

C Role of VBDC as a Monomer Electron Donor

In Part B, it is suggested that VBDC perhaps played the role as electron donor monomer. To our knowledge, the compounds containing N,N-diethyldithiocarbamate group has been scarcely employed as ED in the LCP of isobutene. In order to avoid the stabilizing effect of the counter ion from the initiator moiety, the cumyl chloride is selected and BDC is used as model reagent of VBDC. It is shown in the Table 2, the MWD of the control polymer (Run V4-7) is very broad and the corresponding GPC trace is bimodal, while the MWDs of other samples (V4-2, V4-3 and V4-4) are comparatively narrow and unimodal. This fact suggests that VBDC functions both as a monomer and also as an electron donor in this case.

Table 2. Comparison of VBDC with BDC in the Polymerization of IB Initiated by TiCl₄ / CumCl⁽¹⁾

Run	CumCl, mmol	VBDC, mmol	BDC, mmol	DtBP, mmol	Yield % ⁽²⁾	M _n 10 ⁻⁴	M _w /M _n
V4-2	0.23	1.80	0	0	88.0	1.39	1.44
V4-3	0.23	1.80	0	0.72	89.8	1.39	1.76
V4-4	0.23	0	1.80	0	99.5	1.31	1.35
V4-7	0.23	0	0	0	90.3	1.62	7.68

(1) Isobutene 36.04 mmol, CH₂Cl₂ 10ml, n-hexane 10 ml, TiCl₄ 3.65 mmol, Temperature - 80, Polymerization Time 120 min, terminated by methanol. (2) Overall yield for V4-2 and V4-3 (Weight of Polymer / Weight of Isobutene and VBDC).

Conclusions

The synthesis of polyisobutene containing N,N-diethyldithiocarbamate groups was achieved by cationic copolymerization of isobutene with VBDC. The results demonstrated that the VBDC plays both roles as a comonomer and as an ED which modifies the MWD as well as the M_n of the obtained copolymer.

Acknowledgements

This work is based on research supported by the Foundation for University Key Teacher by the Ministry of Education of the People's Republic of China.

References

1. Faust R, Kennedy J P. *J Polym Sci, Chem Ed*, 1986,25:1847.
2. Kennedy J P, Bela Ivan. *Designed Polymers by Carbocationic Macromolecular Engineering-Theory and Practice*. Hanser Publishers; 1992.
3. Matyjaszewski K. *Cationic Polymerizations, Mechanisms, Synthesis and Applications*. Marcel Dekker Inc; 1997.
4. Bernadette Charleux, Faust R. *Advances in Polymer Science*, Vol 142. Springer-Verlag, 1999.
5. Daniela Held, Bela Ivan, Axel H. E. Muller, Feike de Jong, Chapter 6 in "Cationic Polymerization Fundamentals & Applications"; ACS Series 665, 1997.
6. Bela Ivan, Joseph P. Kennedy, *Macromolecular Design of Polymeric Materials*, Marcel Dekker Inc., Chapter 4, 1997.
7. Judit E. Puskas, Martin Grasmuller, *Macromol. Symp.* 132, 117-126(1998).
8. Takayuki Otsu, Akira Kuriyama. *Polym Bull*, 11:135(1984).
9. Takayuki Otsu, Keiji Yamashita, Kazuichi Tsuda. *Macromolecules*. 1986, 19:287.
10. Mishra M. K., Kennedy J. P., *J. Macromol. Sci-Chem*, A24, 933(1987).
11. H. C. Brown, M. H. Rei., *J. Org. Chem.*, 31, 1090(1966).
12. Milklos Zsuga, J. P. Kennedy, *Polym. Bull.*, 21, 5(1989)
13. B. de Boer, H. K. Simmon, M. P. L. Werts, etc, *Macromolecules*, 33, 349 (2000).