Atom Transfer Radical Polymerization of Butadiene Initiated by Benzyl Chloride/MoCl$_5$ Substituted by 1-octanol/PPh$_3$

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A novel initiator system, benzyl chloride/MoCl$_5$ substituted by 1-octanol/triphenyl phosphine (PPh$_3$), was applied to the atom transfer radical polymerization (ATRP) of butadiene. The characterization revealed the linear increase of the number average molecular weight with the monomer conversion and the rather wide molecular weight distributions of the polymerization products. The microstructure of the butadiene was detected by IR and ^{1}H-NMR. The chlorine atom at ω–end group of the polymer and the change of valence states of molybdenum detected by UV–Vis spectra revealed that the polymerization accorded primarily with the mechanism of ATRP.

Keywords: Atom transfer radical polymerization, Butadiene, Molybdenum

1 Introduction

Obtaining well-defined macromolecular architectures using controlled polymerization techniques has been one of the most important goals of both the academic and industrial laboratories. ATRP is a robust and versatile technique accurately controlling the chain length and polydispersity index (PDI = Mw/Mn) of the polymer, and can be used to synthesize well-defined copolymer as well. As a multicomponent system, the reactive system of ATRP is mainly composed of the monomer, the initiator, the catalyst and some additives. ATRP has now been one focus of the extensive research attention because of its easy experimental setup, use of readily accessible and inexpensive catalysts and simple commercially available or easily prepared initiators (1–3).

A number of low oxidation state metal complexes (3), such as ruthenium (II), copper (I), iron (II) and nickel (II), are known to be effective ATRP catalysts. Inside them, the most utilized catalyst systems are Cu(I) based systems first developed by Matyjaszewski (4). Nevertheless, there are only a few reports about Mo(V) based systems. A series of lithium molybdate(V) complexes of general formula [LiMo(NAr)$_2$($C-N$)R] ($C-N$=C$_6$H$_4$(CH$_2$-NMe$_2$)-2; wherein R = ($C-N$), Me, CH$_2$SiMe$_3$, p-tolyl) have been used in the ATRP of styrene with benzyl chloride as the initiator (5). However, the products had relatively high polydispersities (Mw/Mn = 1.5–1.7) and the efficiency of the benzyl chloride initiator was rather poor (6–18%). In recent contributions, a family of MoIII/MoIV complexes, including cyclopentadienyl complexes (6–8), phosphine containing chloride complexes (9), have been reported for the controlled radical polymerization of styrene, methyl acrylate and butyl acrylate.

Currently, ATRP has been applied to a wide variety of monomers including styrenics, (meth)acrylates and many functional monomers (10). Recently, Ayusman Sen (11–14) and others (15–16) have demonstrated that acrylates can be radically copolymerized with 1-alkenes by ATRP. However, the polymerization of butadiene is slight. The authors found only one reference in literature (17) about ATRP of butadiene by using MoO$_2$Cl$_2$/triphenyl phosphine as the catalyst and the organic halide compounds such as methyl 2-chloropropionate, CCl$_4$, 1,4-dichloromethyl benzene, 1-phenylethyl chloride and benzyl chloride as initiators.

In this work, MoCl$_5$ substituted by 1-octanol (MoCl$_3$(OC$_8$H$_{17}$)$_2$) and triphenyl phosphine (PPh$_3$) are used as catalyst and ligand of the ATRP of butadiene. The primary aim of the study is to explore a possibility in performing ATRP of butadiene (Bd) using an easily accessible catalyst system with good dissolvability in the organic solvent. The role of reaction parameters on monomer yield, molecular weight and polydispersity index of the polymerized butadiene are investigated.

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2 Experimental

2.1 Materials

Butadiene was distilled from a 4A molecular sieve. Toluene (AR, Shanghai Chemical Reagent Co.) was purified by re-fluxing over metal sodium in nitrogen atmosphere. Triphenyl phosphine (AR, Shanghai Chemical Reagent Co.) was recrystallized from ethanol. Benzyl chloride (AR, Beijing Chemical Industrial Co.) was purified by distillation under reduced pressure.

MoCl$_5$ substituted by 1-octanol, MoCl$_3$(OC$_8$H$_{17}$)$_2$, was prepared by the reaction of MoCl$_5$ (AR, Beijing Chemical Industrial Co.) and 1-octanol (AR, Shanghai Chemical Reagent Co.) at 30°C under nitrogen. The mole ratio of MoCl$_5$ to 1-octanol was 1:4; produced hydrochloric acid was removed under vacuum, and the number of Cl in MoCl$_5$ substituted by 1-octanol was detected by titration.

2.2 General Procedure for Polymerization

The flask was sealed with a rubber septum and was cycled between vacuum and nitrogen at 120°C for 2 h, using a high purity nitrogen gas (99.99%). After that, the solution containing monomer, initiator, ligand and solvent was de-gassed by nitrogen purging for 15 min before injected to the reaction flask using a syringe. The reaction flask was then placed in a preheated oil bath at a desired temperature. At some given time, a given volume reactive solution was removed by a syringe. The polymer was precipitated into a large amount of ethanol. The dried product was then characterized by a gravimeter and GPC.

2.3 Measurements and Analysis

Molecular weights and their distributions were measured using GPC with a Shimadzu system composed of a set of KF-1, KF-2, KF-3, KF-4, KF-6 microstyragel columns in tetrahydrofuran with polystyrene standard calibration. FT-IR spectra were recorded on a Nicolet FT-IR-Magna-750 spectrophotometer using KBr pellets. The content of the polybutadiene structure unit was detected by the following (18):

$$\text{Content of cis-1, 4 PB} = 17667 D_{738}/A;$$
$$\text{Content of trans-1, 4 PB} = 4741.4 D_{967}/A;$$
$$\text{Content of 1, 2 PB} = 3673.8 D_{911}/A,$$

Wherein $A = 17667 D_{738} + 4741.4 D_{967} + 3673.8 D_{911}$, $D = Log I_0/I$, where I_0 was the intensity of incident light, I was the intensity of transmitted light in that wavelength.

^{1}H-NMR spectra were measured in CDCl$_3$, using tetramethylsilane as internal reference with a Bruker MSL-300 NMR spectrometer.

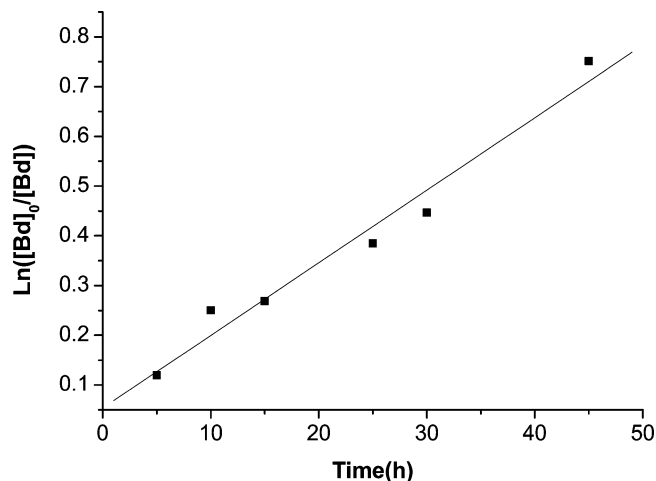The UV-VIS spectra were obtained with a Tu-1800PC spectrophotometer.

Fig. 1. Plot of Ln([M$_0$]/[M]) vs. polymerization time for the ATRP of butadiene in toluene. [Ph· CH$_2$Cl]/[MoCl$_3$(OC$_8$H$_{17}$)$_2$] /[P(Ph)$_3$]/ [Bd] = 1/1/3/200, [Bd]$_0$ = 2.19 M, T = 120°C.

3 Results and Discussion

3.1 Butadiene Polymerization

A novel initiator system Ph· CH$_2$Cl /MoCl$_3$(OC$_8$H$_{17}$)$_2$ /PPh$_3$ was used for the ATRP of butadiene. Figure 1 presents the kinetics of polymerization of Bd in toluene at 120°C. As shown, ln([M$_0$]/[M]) increased continuously with time, and the semi-logarithmic kinetic plot could be approximately fit to a line, which indicates an approximately constant concentration of growing radical.

Figure 2 was the GPC curves of polybutadiene under different monomer conversations. The monomer conversion and molecular weights increased with reaction time. Figure 3 showed a linear dependence of Mn with conversion, while
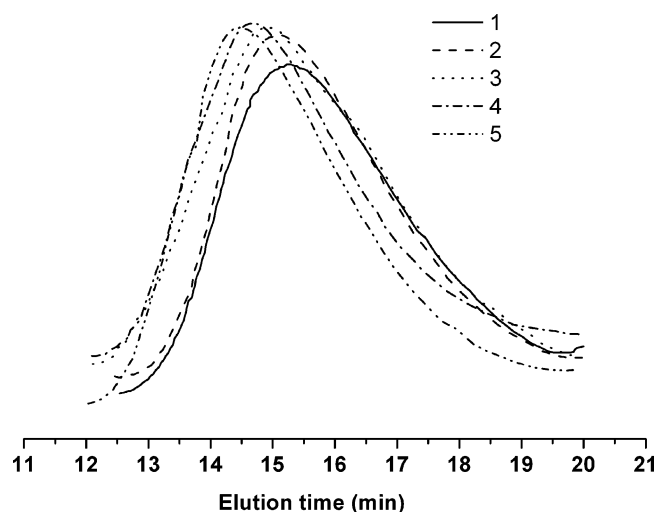

Fig. 2. GPC curves of polybutadiene under different monomer conversation (sample 1 was 11.3%; sample 2 was 22.1%; sample 3 was 31.9%; sample 4 was 36.0%; sample 5 was 52.8%).
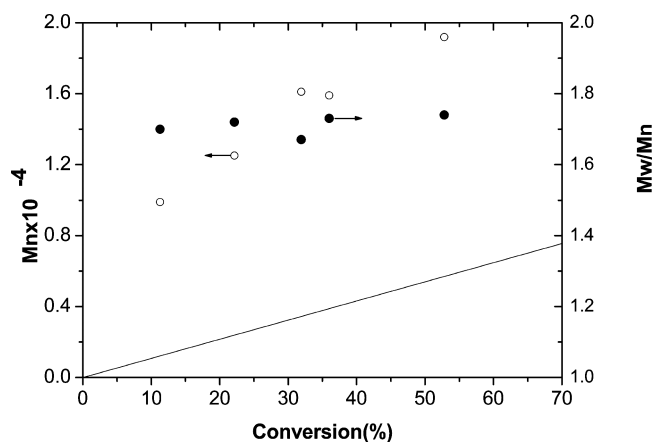
Fig. 3. Dependence $M_{n,GPC}$ and Mw/Mn on conversion in ATRP of butadiene. The conditions were the same as Figure 1. (○) Mn; (●) Mw/Mn; ____ theoretical valued Mth (assuming a "living" condition).

Table 1. The influence on conversion, $M_{n,GPC}$ and Mw/Mn by different initiator system

Conditions	*Ph· CH$_2$Cl/MoCl$_3$ (OC$_8$H$_{17}$)$_2$:P(Ph)$_3$:Bd = 1:1:3:200*	*Ph· CH$_2$Cl: Bd=1:200*	*Bd*
Polymerization time (h)	15.50	62.27	62.27
Conversion(%)	23.6	4.8	4.8
$M_n \times 10^{-4}$	1.24	9.88	8.86
M_w/M_n	1.75	2.44	2.58

Condition: $[Bd]_0 = 2.19M$, $T = 120°C$, solution was toluene.

the polydispersity (Mw/Mn ≈ 1.7) was rather wide and kept almost constant during the polymerization. As can be seen, the measured molecular weights were much greater than those obtained from the theoretical valued M_{th} at low monomer conversion. This fact resulted from the period to reach the equilibrium between the active propagation species and the dormant species and the consequently high concentration of the active propagation species at the beginning of the polymerization.

The efficiency of the benzyl chloride initiator was about 20% in this catalyst system, a little bigger than that of the lithium molybdate complexes catalyst system (4). Concerning the initiator type, it was believed that the ideal initiator should have a similar chemical structure with the monomer. Unfortunately, the suitable initiator for butadiene has not been identified till now. In this work, polymerization of butadiene with CCl$_4$, 1-phenylethyl chloride and 2-chloropropionic acid methyl ester were attempted, respectively. However, no significant improvement in terms of controlled polymerization was observed. These results indicated that some side reactions had participated with the ATRP of Bd. Poorly controlled polymerization in this work may be associated with the effects of reaction parameters on the rate of activation, deactivation and propagation steps, which were inherently versatile.

In order to verify the "living polymerization" character of this polymerization system, the thermal polymerization of butadiene, the polymerization of butadiene initiated by Ph· CH$_2$Cl and the Ph· CH$_2$Cl/MoCl$_3$(OC$_8$H$_{17}$)$_2$/PPh$_3$ system were, respectively in toluene at 120°C. The influence on conversion, molecular weights and polydispersities index by different initiator system are shown in Table 1.

As butadiene polymerization initiated by heat energy and Ph· CH$_2$Cl at 120°C, only a trace amount of product was obtained. Moreover, the molecular weights and the polydispersities were higher than those of the

Ph· CH$_2$Cl/MoCl$_3$(OC$_8$H$_{17}$)$_2$/PPh$_3$ initiator system. That means the two kinds of polymerization were ordinary radical polymerization. But the product yield of the Ph· CH$_2$Cl/MoCl$_3$(OC$_8$H$_{17}$)$_2$/PPh$_3$ initiator system could reach 23.6% after 15.5 h ,the Mn was close to M_{th} (assuming a "living" condition) and Mw/Mn was narrower than those of the other two initiator systems, which revealed that the "living"/controlled radical polymerization of butadiene could be carried out in toluene at 120°C with the Ph· CH$_2$Cl/MoCl$_3$ (OC$_8$H$_{17}$)$_2$/PPh$_3$ system.

It was worth comparing the above results with those obtained in the literature concerning the ATRP of isoprene with CuBr/N,N,N',N',N"-pentamethyl diethylenetriamine catalyst and ethyl bromopropionate initiator. The reported ATRP of isoprene in a bulk system resulted in only a trace amount of product, irrespective of reaction parameters (19). At the same time, the polydispersities of product was up to around 2.0. In this paper, the conversion of polybutadiene could reach 23.6% after 15.5 at 120°C. The polydispersities of this system was lower than 2.0.

The FTIR spectrum of the polybutadiene (Fig. 4) showed several characteristic absorption peaks corresponding to
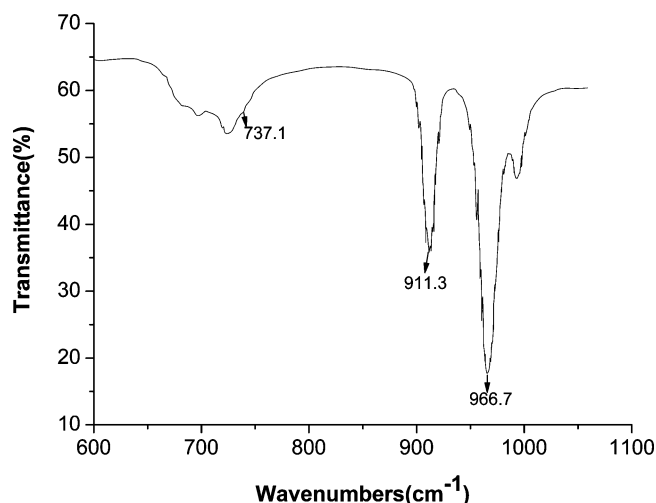

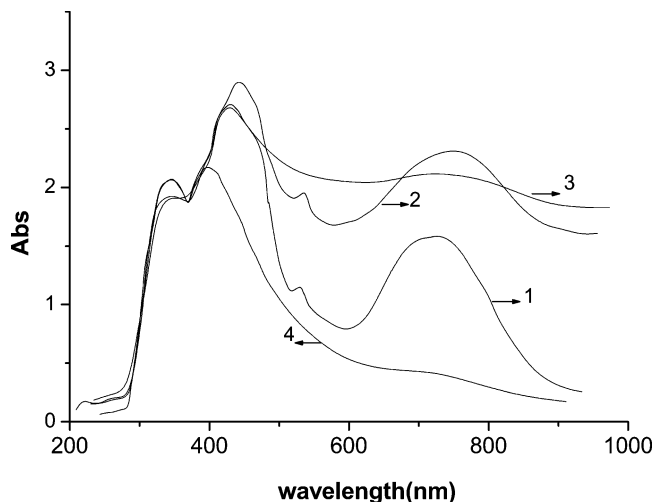**Fig. 4.** The FTIR spectrum of polybutadiene.

Fig. 5. UV-Vis spectra of $MoCl_3(OC_8H_{17})_2$ (1), $MoCl_3(OC_8H_{17})_2/P(Ph)_3$ (2), $MoCl_3(OC_8H_{17})_2/P(Ph)_3/Ph\cdot CH_2Cl$ (3) and Bd/ $MoCl_3(OC_8H_{17})_2/P(Ph)_3/Ph\cdot CH_2Cl$ (4) in toluene.

the chemical bonds in polybutadiene molecules, including the peaks at 966.7 cm^{-1} (assigned to γ_w(CH) rock vibration of CH=CH of trans-1,4 butadiene structural unit), 911.3cm^{-1} (assigned to $\delta_{=C-H}$ deformation of CH=CH of 1,2-butadiene structural unit) and 737.1 cm^{-1} (assigned to δ_{-C-H}, out-of-plane deformation of CH=CH of cis-1,4 butadiene structural unit). The content of cis-1,4, trans-1,4 and 1,2- butadiene structural unit were 22.1%, 58.4% and 19.5%, respectively. The result was similar to that from ^{1}H-NMR of the PBd (the content of 1,4 was 83.1% and 1,2 was 16.9% calculated according to reference (20)). The

microstructure of PBd was similar to that generally obtained from the conventional free radical polymerization (21).

3.2 Analysis of Polymerization Mechanism

Figure 5 showed the UV-Vis spectrum of toluene solution of $MoCl_3(OC_8H_{17})_2$, $MoCl_3(OC_8H_{17})_2/P(Ph)_3$, $MoCl_3(OC_8H_{17})_2/P(Ph)_3/Ph\cdot CH_2Cl$ and Bd/MoCl$_3$ $(OC_8H_{17})_2/P(Ph)_3/Ph\cdot CH_2Cl$. In the UV-Vis spectrum of $MoCl_3(OC_8H_{17})_2$, the characteristic absorption bands for Mo^{5+} near 430 nm and 730 nm and for Mo^{4+} near 510 nm, could be found (21). The presence of Mo^{4+} was probably due to a little deoxidized reaction of $MoCl_3(OC_8H_{17})_2$ which took place during the operation of putting up the MoCl$_5$ substituted by 1-octanol solution. The absorption peak of 730 nm was caused by the d-d transition of Mo atom in $MoCl_3(OC_8H_{17})_2$. After PPh$_3$ was added, the absorption at 730 nm became weaker, perhaps because of the changing of ligand with the competition coordination on Mo atom by PPh$_3$ and 1-octanol. At the same time, the absorption at 430 nm increased, which indicated the increase of Mo^{4+} content. After the solution of Bd/$MoCl_3(OC_8H_{17})_2/P(Ph)_3/Ph\cdot CH_2Cl$ in toluene had been placed in a oil bath at 90°C for 5 h, the absorption at 730 nm became smooth, 430$\sim$ 460 nm became weaker in its UV spectrum. At the same time, yellow deposit arose in the solution, which accounted for the content of Mo^{6+} increasing. These results revealed that Mo^{4+}, Mo^{5+} and Mo^{6+} were in existence together in this reactive system. The valency state of Molybdenum has changed during the reaction.
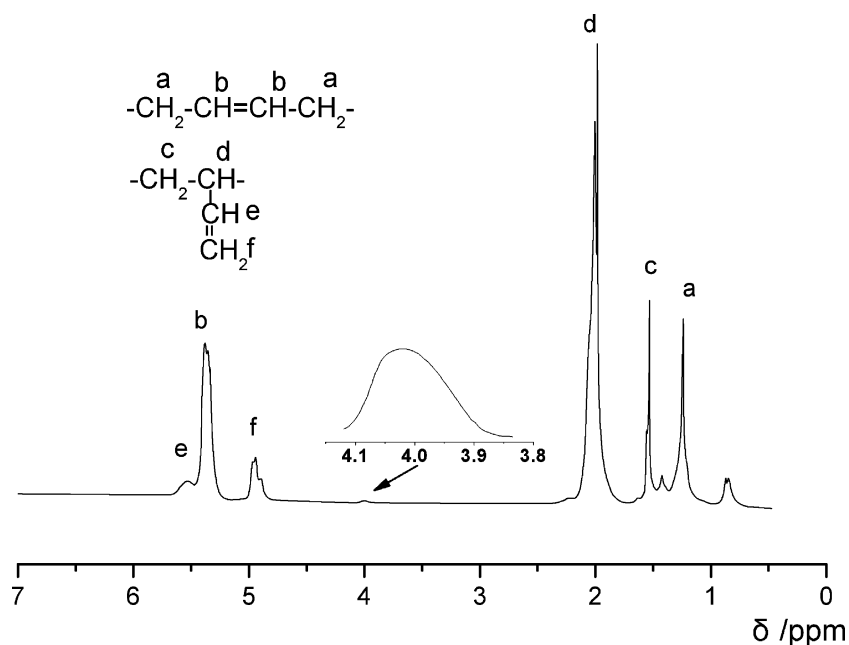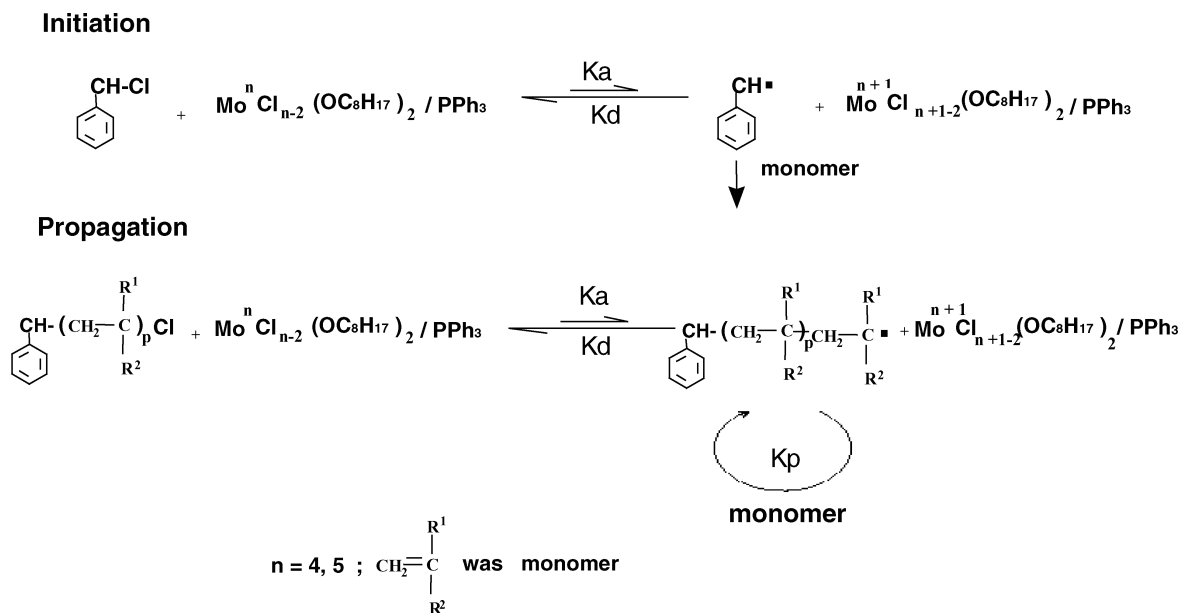

Fig. 6. ^{1}H-NMR spectrum of the polybutadiene initiated by $MoCl_3(OC_8H_{17})_2/P(Ph)_3/Ph\cdot CH_2Cl$.

Initiation

$$CH\text{-}Cl \;\; + \;\; Mo^{n}Cl_{n-2}(OC_8H_{17})_2 / PPh_3 \quad \underset{Kd}{\overset{Ka}{\rightleftharpoons}} \quad CH\bullet \;\; + \;\; Mo^{n+1}Cl_{n+1-2}(OC_8H_{17})_2 / PPh_3$$

monomer

Propagation

$$CH\text{-}(CH_2\text{-}C)_p Cl \;+\; Mo^{n}Cl_{n-2}(OC_8H_{17})_2 / PPh_3 \quad \underset{Kd}{\overset{Ka}{\rightleftharpoons}} \quad CH\text{-}(CH_2\text{-}C)_p CH_2\text{-}C\bullet \;+\; Mo^{n+1}Cl_{n+1-2}(OC_8H_{17})_2 / PPh_3$$

with R^1 / R^2 substituents

Kp

monomer

$$n = 4, 5 \; ; \quad CH_2{=}C \text{ (with } R^1, R^2\text{)} \quad \text{was monomer}$$

Sch. 1. The polymerization mechanism of of the butadiene by $Ph\cdot CH_2Cl/MoCl_3(OC_8H_{17})_2/PPh_3$ initiation system.

A signal at δ 4.0 ppm corresponding to the terminal proton adjacent to the chlorine atom at ω –end group is also observed in the ^{1}H-NMR (Fig. 6) of the polybutadiene obtained. All this implied that the oxidation and deoxidized reaction of $MoCl_3(OC_8H_{17})_2$ occurred in agreement with the mechanism of ATRP.

So, the mechanism of the butadiene by $Ph\cdot CH_2Cl/MoCl_3(OC_8H_{17})_2/PPh_3$ initiation system might be deduced as is shown in the following schematic illustration.

When $MoCl_3(OC_8H_{17})_2$ was reacted with $Ph\cdot CH_2Cl$, an electron transfer reaction could occur as shown in Scheme 1, in which the Mo(V) or Mo(IV) were oxidized to Mo(VI) or Mo(V), respectively with concomitant formation of a benzyl radical. This reaction was typical for the initiation step in ATRP reactions. The formed benzyl radicals reacted with the alkene (diolefin) to produce polymer chain radicals. Both radicals can react back with $Mo^{n+1}Cl_{n+1-2}(OC_8H_{17})_2/PPh_3$ to give $Mo^{n}Cl_{n-2}(OC_8H_{17})_2/PPh_3$ and the corresponding alkyl halide (dormant species, Scheme 1). More than one kind of reversible oxidation and reduced reaction have occurred in this reactive system which may be another reason for the rather wide molecular weights polydispersities.

4 Conclusions

Atom transfer radical polymerization of butadiene was successfully initiated by the $Ph\cdot CH_2Cl/MoCl_3(OC_8H_{17})_2/PPh_3$ system. The almost linear first order rate plots of kinetics and the linear increase of the number average molecular weight with monomer conversion demonstrated its characteristic of "quasi-living" radical polymerization. However, rather wide molecular weight distributions indicated the control ability of this polymerization system should be further improved. PBd was atactic polymer, as detected by IR. The primary mechanism of reaction was proved according to the mechanism of ATRP.

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