Atom Transfer Radical Polymerization of Butadiene Using MoO_2Cl_2/PPh_3 as the Catalyst

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ABSTRACT: Atom transfer radical polymerization has been used to successfully synthesize polybutadiene. This was achieved by using MoO_2Cl_2/triphenyl phosphine as the catalyst and the various organic halide compounds such as methyl-2-chloropropionate, CCl_4, 1,4-dichloromethyl benzene, 1-phenylethyl chloride, and benzyl chloride as initiators. The monomer conversion increased up to 50% with polymerization time. The polydispersity indices of the polymers were as high as above 1.5. However, the polymerizations were controlled and the polydispersity indices of the polymers were less than 1.5 throughout the polymerization in reverse atom transfer radical polymerization. The chemical structure of the polymer obtained was characterized by ^{1}HNMR and FTIR. The valency states of molybdenum in this reactive system were detected by UV–vis spectra. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 3517–3522, 2007

Key words: atom transfer radical polymerization; styrene; butadiene; molybdenum

INTRODUCTION

Atom transfer radical polymerization (ATRP) has attracted much attention over the past decade for providing a simple and robust route to synthesize well-defined and low-molecular-weight distribution polymers.[1–3] It is generally accepted that ATRP proceed via a reversible redox process between the polymer end (P_nX) and the metal catalyst (M_t^n) based on Cu, Fe, Ni, and Ru with a suitable phosphine- or nitrogen-based ligand (Scheme 1).
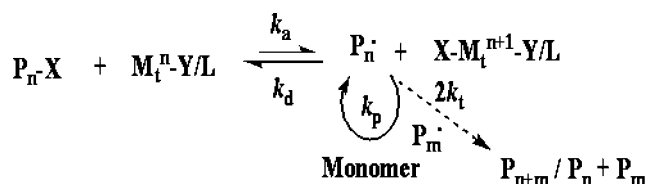
The polymerization process involves a reversible equilibrium between the propagating radical and the dormant species. The Cu (I)-based catalysts are superior in ATRP in terms of versatility and cost. In recent years, the molybdenum complexes have been exploited to act as a candidate catalyst for ATRP because of their variable oxidation states, despite their sensitivity to air and protic compounds. For example, lithium molybdate(V) complexes of general formula [LiMo(NAr)$_2$(C—N)R] (C—N=C_6H_4(CH_2—NMe_2)-2; R = (C—N), Me, CH_2SiMe_3, p-tolyl) have been used in the ATRP of styrene with benzyl chloride (BCl) as the initiator.[4] Relatively high polydispersities (M_w/M_n = 1.5–1.7) were obtained, and the efficiency of the BCl initiator was rather poor (6–18%). Poli and co-

workers[5] have applied the analysis of bond dissociation energies to the choice of half-sandwith Mo(III) system suitable for controlling styrene polymerization by either the stable free radical polymerization or ATRP. They[6] also reported the controlled radical polymerization of styrene with new CpMoCl$_2$(R$_2$-dad) complexes (R$_2$-dad = RN=CH—CH=NR, with R = Ph, p-tol, 2,6-^{i}Pr$_2$C$_6$H$_3$ and ^{i}Pr) under typical stable free radical polymerization and ATRP conditions. In another article,[7] they presented that CpMoCl$_2$(iPr$_2$-diazadiene) is an efficient catalyst for the controlled free radical polymerization of methyl acrylate, butyl acrylate, and styrene. In a recent contribution, polystyrene was obtained by a controlled polymerization procedure, with control being exerted by easily accessible numerous compounds of type phosphine containing MoIII/MoIV complexes, MoCl$_3$L$_3$, and MoCl$_4$L$_n$ (L = ethers, thioethers, phosphines, etc.; n = 2 or 3).[8]

To date, ATRP has been successful in controlling the polymerization of styrene and (meth)acrylates, (meth)acrylamides, acrylonitriles, and the other monomers that contain substituents that can stabilize the propagating radicals.[3] Sen and coworkers[9] reported copper-mediated controlled copolymerization of methyl acrylate with nonpolar 1-alkenes ranging from ethene to 1-octene under mild conditions to afford random copolymers and copolymerization of methyl acrylate with norbornene derivatives initiated by CuBr, ethyl 2-bromopropionate, and N,N,N',N',N''-pentamethyl-diethylenetriamine by ATRP.[10] Klumperman and coworkers[11] also reported atom transfer radical copoly-

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$$P_n\text{-}X \; + \; M_t^n\text{-}Y/L \; \underset{k_d}{\overset{k_a}{\rightleftharpoons}} \; P_n^{\cdot} \; + \; X\text{-}M_t^{n+1}\text{-}Y/L$$

$$P_m^{\cdot}$$

$$2k_t$$

$$\text{Monomer} \quad P_{n+m} / P_n + P_m$$

Scheme 1 Generally accepted mechanism of ATRP.

merization of methyl acrylate with 1-octene using ethyl 2-bromoisobutyrate as initiator and using CrBr and 4,4-dinonyl-2,2-bipyridine as catalyst. However, to the best of our knowledge, ATRP of butadiene has not been reported as yet. It is known that the butadiene polymerization suits radical, anionic, and coordination mechanism. In addition, Mo (VI) compounds, such as MoO_2Cl_2 and $MoO_2Cl(OR)$, are an effective catalyst for coordination polymerization of butadiene. This strongly urges us to investigate whether MoO_2Cl_2 could be used as the catalyst for the ATRP of butadiene.

In this article, a novel catalyst system, i.e., MoO_2Cl_2/triphenyl phosphine (PPh_3), has been applied in the radical polymerization of butadiene. The employed initiators involve methyl-2-chloropropionate (MBP), CCl_4, 1,4-dichloromethyl benzene (1,4-DClMP), 1-phenylethyl chloride (1-PECl), and BCl. It has been confirmed that the polymerization of butadiene at our experimental conditions proceeded via an ATRP mechanism.

EXPERIMENTAL

Materials

Butadiene (Bd) was dried over 4 Å molecular sieve and distilled prior to use. PPh_3 was purified by recrystallization from ethanol. MBP, CCl_4, 1,4-DClMP, 1-PECl, and BCl were purchased and used as received. Toluene was refluxed and distilled from Na/benzophenone under dry nitrogen. The MoO_2Cl_2 solution was prepared by mixing acetic ether/$MoCl_2O_2$ (1 : 10) and diluting with toluene.

Polymerization procedure

A flask was sealed with a rubber septum and was cycled between vacuum and dry nitrogen at 120°C for 2 h. A solution containing monomer, initiator, catalyst, and ligand was degassed by bubbling nitrogen for 15 min, and then injected into the reaction flask via a syringe. The flask was then placed in a preheated oil bath. During the reaction, samples were taken periodically. The polymer was precipitated into a large amount of ethanol, filtered, washed with methanol, and dried in vacuum. The monomer conversions were determined gravimetrically.

Characterization

The number average molecular weights (M_n) and polydispersity indices (PDIs) of the polymer samples were measured using GPC with a SHIMADZU system composed of a set of KF-1, KF-2, KF-3, KF-4, and KF-6 microstyragel columns in tetrahydrofuran, calibrated with narrow polystyrene standard. ^{1}HNMR spectra were recorded on an AL-spectrometer 300 MHz FTIR systems-JEOl spectrometer in $CDCl_3$ using tetramethylsilane as internal reference. FTIR spectra were measured on a Nicolet FTIR-Magna-750 spectrophotometer using KBr pellets.

RESULTS AND DISCUSSION

A novel catalyst system $MoCl_2O_2/PPh_3$ was used to initiate the ATRP of butadiene. Figure 1 presents the kinetic plots of ln ($[M]_0/[M]$) versus time for polymerization of butadiene with $CCl_4/MoCl_3(OC_8H_{17})_2/PPh_3$ initiator system in toluene at 120°C. The catalyst system has good solubility in this butadiene polymerization system. The straight semilogarithmic kinetic plot of ln ($[M_0]/[M]$) versus time showed linear first-order rate plots.

Figure 2 shows a linear dependence of M_n with conversion. The polydispersity index ($M_w/M_n = 1.7$) was rather wide and it almost remained unchanged during the polymerization. The efficiency of the initiator was about 35%.

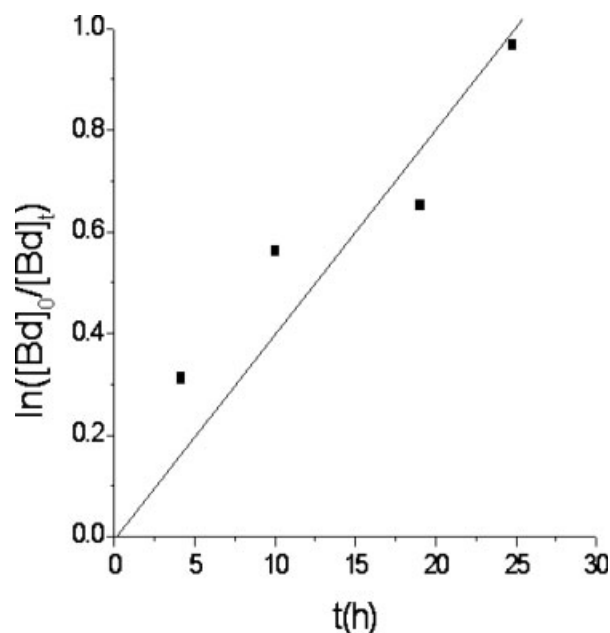Concerning initiator type, it was believed that the initiator should be ideally similar to the monomer in

Figure 1 Kinetics for the ATRP of butadiene in toluene at 120°C. $CCl_4/MoCl_2O_2/P(Ph)_3/[Bd] = 1/1/2/200$ (molar ratio).
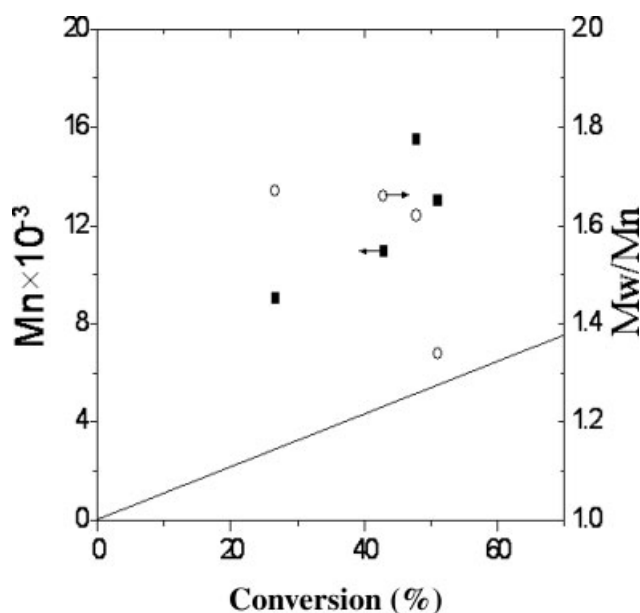
Figure 2 M_n and M_w/M_n vs conversion for ATRP of butadiene, (■) M_n; (○) M_w/M_n; ___M_{th}.

term of chemical structure. Unfortunately, a suitable initiator for butadiene has not been identified. In this work, the various ATRP initiators were employed, such as MBP, 1,4-DClMP, and 1-PECl. The results are listed in Table I.

As can be seen, the number-average molecular weights of the polymers are much higher than those theoretical values (M_{th}) at low monomer conversion (Entries 1, 4, and 5) in the case of 1,4-DClMP and 1-PECl, while the M_ns are close to M_{th} at high monomer conversion (Entries 2, 3, and 6). This fact implies that the efficiencies of 1,4-DClMP and 1-PECl were poor at low monomer conversions. This suggests that it would need a period to reach the equilibrium between the active propagation species and the dormant species; thus, the number of active propagation species at the beginning of the polymerization was low. As far as CCl_4 and MBP are concerned, the M_ns

of the polymers were much higher than the M_{th} throughout the polymerization (Fig. 2 and Entries 7–9 in Table I), which indicates that the efficiencies of CCl_4 and MBP are lower than those of 1,4-DClMP and 1-PECl.

The data listed in Table I also show that the PDIs of the polymers are broad using 1,4-DClMP and 1-PECl as initiators. Although the substitution of them by CCl_4 and MBP can lower PDIs to a certain extent, the values of the PDIs are still high. In other words, no significant improvement in controlling butadiene polymerization is observed by changing the structures of the initiators. Poor 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.

For the sake of the confirmation of the mechanism of the polymerization reaction, we characterize the structure of polybutadiene using ^{1}HNMR technique. As shown in Figure 3, a small absorptions signal at $\delta 3.95$ ppm corresponding to the terminal proton adjacent to the chlorine atom at ω-end group was observed, which confirms that this polymerization process undergoes an ATRP mechanism.

We also attempted to carry out the reverse ATRP of butadiene using AIBN as the initiator, and the results are shown in Figures 4 and 5.

It is obvious that there is a linear relationship between ln ($[M]_0/[M_t]$) and reaction time. The first-order kinetics implied that the concentration of the free radical remained constant during the polymerization. The molecular weights linearly increased with monomer conversion. However, they were higher than those predicted by the ratio of the consumed monomer to initiator, indicating that the number of the polymer chains produced was less than that predicted. PDIs remained less than 1.5 throughout the polymerization. A signal at $\delta 3.95$ ppm corresponding to the terminal proton adjacent to the chlorine atom at ω-end group is also observed in the ^{1}HNMR of the

TABLE I
Results of ATRP of Butadiene at 120°C

Entry	Initiator[a]	Time (h)	Conversion (%)	M_{th}[b] $\times 10^4$	M_n[c] $\times 10^4$	PDIs[c]
1	1,4-DClMP	10.0	24.0	0.26	0.60	1.73
2	1,4-DClMP	19.0	50.4	0.54	0.66	1.84
3	1,4-DClMP	33.9	57.8	0.62	0.70	1.97
4	1-PECl	4.00	19.6	0.21	0.55	1.73
5	1-PECl	10.0	29.3	0.32	0.66	1.83
6	1-PECl	33.9	52.4	0.57	0.74	1.85
7	MBP	10.0	22.2	0.24	1.05	1.65
8	MBP	19.0	43.2	0.46	1.58	1.49
9	MBP	33.9	51.1	0.55	1.62	1.55

[a] $[Bd]/[I]/[MoCl_2O_2]/[PPh_3] = 200/1/1/3$.
[b] $M_{th} = [Bd]/[I] \times$ molecular weight of butadiene $\times$ conversion.
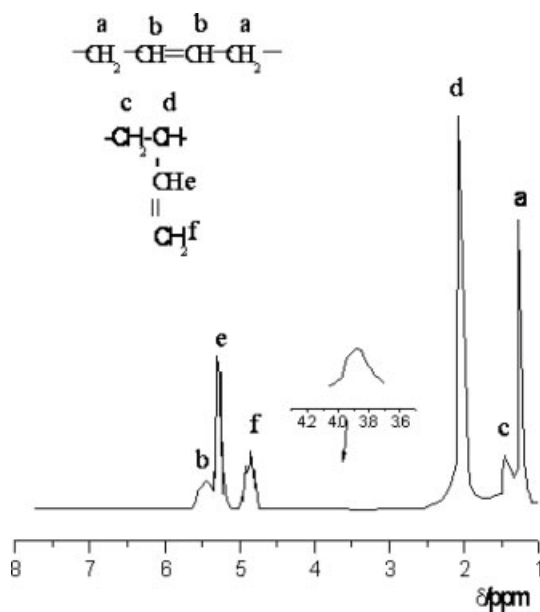[c] Determined by GPC.

Figure 3 ^{1}HNMR spectrum of the polybutadiene initiated by CCl₄.

polybutadiene obtained, which also indicates that the polymerization belongs to a reverse ATRP process.

To investigate a possible influence of thermal polymerization at 120°C, several tests were carried out, and the results are summarized in Table II. When neither BCl/MoO₂Cl₂/PPh₃ nor MoO₂Cl₂/PPh₃ is used, only a trace amount of product yield was obtained. Moreover, the M_n and PDIs were broader than those of the system in the presence of BCl/MoO₂Cl₂/PPh₃. This reveals that the polymerization of butadiene
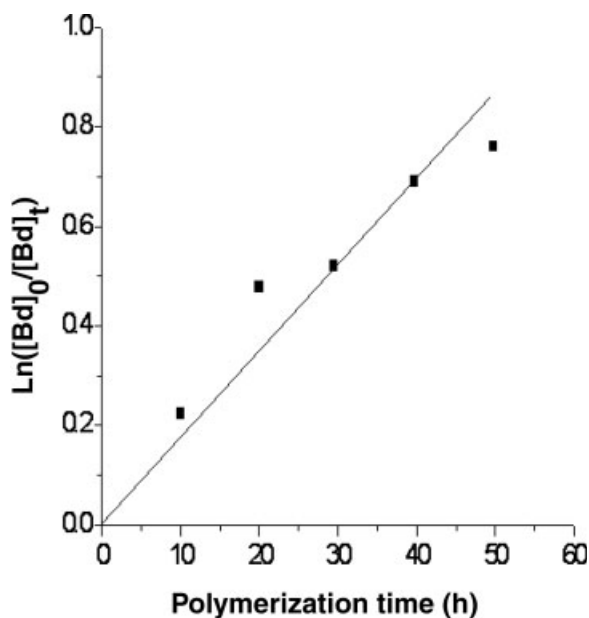

Figure 4 Plots of ln ([M]₀/[M_t]) versus polymerization time. [Bd]/[AIBN]/[MoO₂Cl₂]/[PPh₃] = 200 : 1 : 1 : 2.

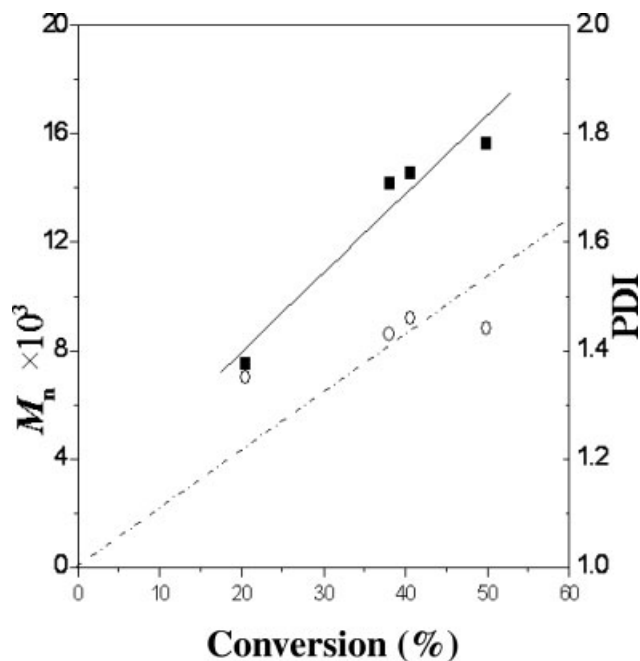**Figure 5** Plots of M_n and PDIs of the polybutadienes versus monomer conversion. (■) M_n; (○) PDIs; (-·-·-·-) $M_{th,}$ [Bd]/[AIBN]/[MoO₂Cl₂]/[PPh₃] = 200 : 1 : 1 : 2.

initiated by BCl with a MoO₂Cl₂/PPh₃ catalyst proceeds via an ATRP process.

A few polymer chemists have reported the ATRP of diene up to now. It is worthwhile to compare their results with that of us. The ATRP of isoprene has been performed in the presence of CuBr/N,N,N′,N′,N″-pentamethyl diethylenetriamine as the initiator and ethyl bromoproprionate as the catalyst and the initiator, respectively.[12] However, only a trace amount of polymer product was attained, irrespective of reaction conditions. The values of PDIs are always around 2.0. However, under our experimental conditions, the conversion of butadiene was more than 50% after 30 h at 120°C and PDIs are less than 1.5 in reverse ATRP.

Figure 6 reveals the FTIR spectrum of the polybutadiene prepared by ATRP. The characteristic absorption peaks corresponding to the different chemical bonds in polybutadiene were observed. The peaks at 966.3, 909.3, 740.1 cm^{-1} assigned to γ_w(CH) rock vibration of CH=CH of tran-1,4 butadiene structural unit, δ=C—H deformation of CH=CH of 1,2-butadiene

TABLE II
Influence of Thermal Polymerization

Conditions	Bd/BCl/MoO₂Cl₂/PPh₃ (200 : 1 : 1 : 3)	Bd/BCl (200 : 1)	Bd
Time (h)	50	62	62
Conversion (%)	34.0	4.8	4.8
$M_n \times 10^4$	0.93	9.88	8.86
PDIs	1.68	2.44	2.58

structural unit), δ—C—H out of plane deformation of CH=CH of *cis*-1,4 butadiene structural unit, respectively. The content of polybutadiene structure unit was determined according to the equation as follows:[13]

content of *cis*-1,4 PB = $17,667.0D_{738}/A$;
content of trans-1,4 PB = $4741.4D_{967}/A$;
content of 1,2 PB = $3673.8D_{911}/A$.

where $A = 17,667.0D_{738} + 4741.4D_{967} + 3673.8D_{911}$, $D = Log\ I_0/I$, I_0 was the intensity of incident light, I was the intensity of transmitted light in that wavelength. From the intensities of these absorptions, the contents of *cis*-1,4, *trans*-1,4, and 1,2-butadiene structural unit in the polymer were determined to be 26.5%, 54.1%, and 19.4%, respectively. Thus, the microstructure of polybutadiene obtained by ATRP is atactic, similar to that of the polymer prepared by the classical free radical polymerization.[14]

In the UV–vis spectrum of $MoCl_2O_2$ in Figure 7, the characteristic absorption bands for Mo^{VI} near 346 nm can be found.[15] As PPh_3 was added, the absorption for Mo^{IV} near 465 nm was increased. The reason may be that the Mo^{VI} was reduced by PPh_3 and the changing of ligand with the competition coordination on Mo atom by PPh_3. After the solution of $MoCl_2O_2/P(Ph)_3/C_6H_5\cdot CH_2Cl$ in toluene has been placed in a oil bath at 100°C for 0.5 h, the absorption bands for Mo^V near 720 nm appeared and the characteristic absorption bands for Mo^{VI} near 346 nm became weaker in its UV spectrum. So, Mo^{IV}, Mo^V, and Mo^{VI} were in existence together in this reactive system. The
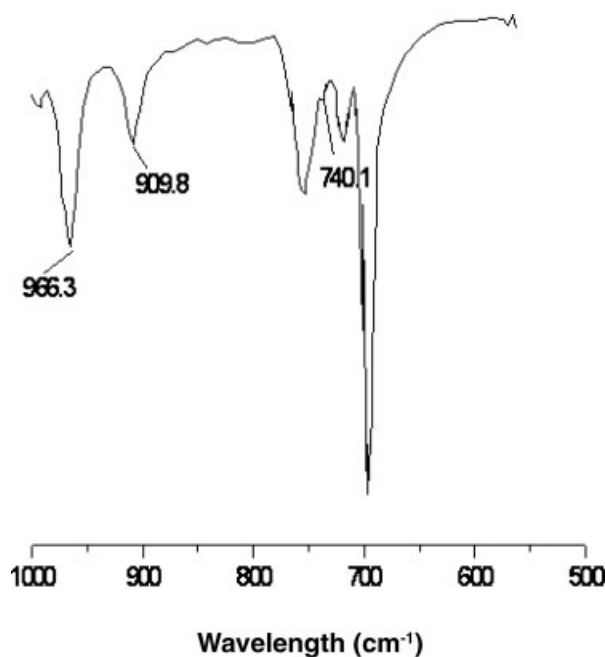

Figure 7 UV–vis spectra of MoO_2Cl_2 (1), $MoO_2Cl_2/P(Ph)_3$ (2), $MoO_2Cl_2/P(Ph)_3/BCl$ (3) in toluene.

valency state of molybdenum has changed during the reaction. These approved that oxidation and deoxidized reaction of $MoCl_2O_2$ had taken place, which might comply with the mechanism of ATRP.

CONCLUSIONS

In conclusions, ATRP has been shown to be successful in synthesizing polybutadiene with predictable molecular weights using a MoO_2Cl_2/PPh_3 catalyst system. Although the PDIs of the polymers are relatively broad, it cannot negate that the polymerization proceeded via an ATRP mechanism, which is verified by the ^{1}HNMR spectrum analysis and the thermal polymerization experiments. Furthermore, in the reverse ATRP, the $\overline{M}_n$s of the polymers gradually increased with monomer conversions and the PDIs of the polymers were less than 1.5, which is a feature of "quasi-living." This indirectly proves that the polymerization reactions were carried out via a reversible ATRP process. Mo^{IV}, Mo^V, and Mo^{VI} were in existence together in this reactive system detected by UV–vis spectra. This approved that oxidation and deoxidized reaction of $MoCl_2O_2$ had taken place, which might comply with the mechanism of ATRP.

Figure 6 The FTIR spectrum of polybutadiene.

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