Ru-알킬리덴 착물 촉매를 이용한 스티렌-부타디엔 고무의 복분해 반응

Tingting Zou*, Bin Jiang*, Shaohui Lin*, and Qinmin Pan*,**,†

*Green Polymer and Catalysis Technology Laboratory, College of Chemistry, Chemical Engineering and
Material Science, Soochow University
**Suzhou Key Laboratory of Green Chemical Engineering, School of Chemical and
Environmental Engineering, Soochow University
(2016년 2월 1일 접수, 2016년 4월 18일 수정, 2016년 5월 7일 채택)

Metathetic Degradation of Styrene-Butadiene Rubber via Ru-Alkylidene Complex Catalyzed Reaction

Tingting Zou*, Bin Jiang*, Shaohui Lin*, and Qinmin Pan*,**,†

*Green Polymer and Catalysis Technology Laboratory, College of Chemistry, Chemical Engineering and Material Science,
Soochow University, Suzhou 215123, Jiangsu Province, People's Republic of China
**Suzhou Key Laboratory of Green Chemical Engineering, School of Chemical and Environmental Engineering,
Soochow University, Suzhou 215123, Jiangsu Province, People's Republic of China
(Received February 1, 2016; Revised April 18, 2016; Accepted May 7, 2016)

Abstract: Metathetic degradation and functionalization of styrene-butadiene rubber (SBR) were performed with allyl hexanoate, allyl chloroacetate, 5-hexenyl acetate and trifluoroethyl methacrylate as chain transfer agents (CTAs) using Grubbs 2nd generation catalyst. It has been demonstrated that the catalyst concentration, CTA concentration and reaction time were major factors influencing the molecular weights and polydispersity indices of targeted telechelic SBR oligomers. Well-defined oligomers with molecular weights ranging from 700 to 36600 g mol^{-1} and polydispersity indices ranging from 1.17 to 4.79 were realized. The structures of the SBR oligomers were determined by FTIR and ^{1}H NMR analyses, which indicated that the functional groups of the CTAs were successfully attached onto the end of the polymer chains. To further investigate the performance of SBR oligomers, differential scanning calorimetry (DSC) analysis was performed, which indicated that the glass transition temperature (T_g) of the metathesis products decreased with longer reaction time.

Keywords: metathetic degradation, functionalization, styrene-butadiene rubber, ruthenium catalyst.

Introduction

Olefin metathesis was initially discovered by Ziegler when he was studying the industrial synthesis of polyethylene. He found that unsaturated carbon-carbon bonds of the olefins were cleaved and rearranged to yield new olefins in the presence of transition metal carbene complexes.[1,2] In the early 1970s, Chauvin proposed a novel metathesis mechanism which is now widely accepted by other chemists and technologists. He suggested that the formation of a metallocarbene sequestered an olefin to form a metallacyclobutane as a viable intermediate.[3] Based on this reaction, a variety of well-defined single component metal carbene complexes such as titanium catalysts,[4-6] tungsten catalysts[7-9] and molybdenum catalysts[10,11] had been developed and widely used in the early years. Nevertheless, these catalysts were shown to require severe reaction conditions, and were extremely sensitive to oxygen and moisture. In the 1990s, Grubbs *et al.* developed the ruthenium-based catalyst (PCy$_3$)$_2$(Cl)$_2$Ru=CHPh (Grubbs 1st generation catalyst) and ruthenium alkylidene containing *N*-heterocyclic carbene (NHC) ligands (Grubbs 2nd generation catalyst) which showed higher stability towards alcohols, amides, aldehydes, and carboxylic acids and displayed high efficiency in olefin metathesis when compared with predecessors.[12-14]

With the progress of catalysis techniques based on different transition metals, the use of olefin metathesis to produce specific compounds has attracted increasing attention in the recent decades. Many different types of alkene metathesis reactions have been used, such as ring-opening metathesis polymerization (ROMP), ring-closing metathesis (RCM), acyclic diene metathesis polymerization (ADMET) and cross-metathesis (CM).[15,16] Various functionalized oligomers, which were found to be very useful as forerunners in the polymeric networks and block copolymers, were successfully synthesized by intermolecular metathetic degradation of unsaturated polymers with the addition of a monoolefin and a metal carbene complex as catalyst.[17-20] The first study regarding metathetic degradation of polybutadiene with monoolefins was reported by Hummel's group in 1970. The reaction was conducted using a tungsten-based catalyst with hex-2-ene as the chain transfer agent (CTA), yielding a mixture of butadiene oligomers.[21] In the 1980s and 1990s, they proceeded to discover that a series of highly end-functionalized telechelics could be produced using Mo and W catalysts with ethylene and octene as CTAs.[22-29] In the 1990s, with the development of the Schrock catalyst, Wagener's group utilized silyl olefins for depolymerization of 1,4-polybutadiene to synthesize perfectly difunctional telechelic polybutadiene oligomers.[30-32] Additionally, Wagener's group recently reported successful depolymerization of polybutadiene with acryloyl chloride via insertion metathesis reaction in the presence of Grubbs 2nd generation catalyst.[33] Natural rubber (NR) with trisubstituted alkene was found to be unsuitable for the metathetic degradation as NR was very sensitive to side reactions and degraded much slower than other disubstituted polyalkenamers in the presence of the classic metathesis catalysts.[24,16,34] With the introduction of Grubbs 2nd generation catalyst characterized by high activity and tolerance towards polymers with trisubstituted alkene,[35] the successful metathetic degradation of natural rubber with various functionalized olefins to obtain well-defined isoprene telechelic oligomers in the presence of ruthenium catalysts was reported.[35-41]

It is of great interest to be able to control the degradation process of SBR to produce functionalized blocks that could be used in synthesizing new materials. However, to date, there have only been a limited number of scientific publications describing the metathetic degradation of SBR. In this study, we investigate the cross-metathesis degradation of SBR with 5-hexenyl acetate, allyl hexanoate, allyl chloroacetate and trifluoroethyl methacrylate as CTAs in the presence of the commercially available Grubbs 2nd generation catalyst. The effects of different CTAs, catalyst efficiency, controlled molar ratio of [-C=C-]:[CTA] and reaction time on molecular weight (M_n) and polydispersity index (PDI) of functionalized telechelic oligomers are also explored.

Experimental

Materials. SBR (M_n=58900 g mol^{-1}, PDI=4.89) containing 11% of styrene, 6.6% of 1, 4-cis units, 69% of 1, 4-trans units and 13.4% of 1, 2-units was purchased from Sinopec Beijing Yanshan Company and purified prior to use. Tricyclohexylphosphine [1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene] benzylidene ruthenium (IV) dichloride (Grubbs 2nd generation catalyst, G2), 5-hexenyl acetate, allyl hexanoate and allyl chloroacetate were purchased from energy chemical (Shanghai, China) and used as received. Trifluoroethyl methacrylate was purchased from Aladdin and used without any purification. 1, 2-dichloroethane was purchased from Shanghai Chemical Reagents Co., Ltd and distilled over CaH$_2$ prior to use.

Analysis and Characterization. ^{1}H NMR analysis was performed to obtain structures of telechelic oligomers synthesized via metathetic degradation of SBR with CTAs. The ^{1}H NMR spectra were recorded on a Bruker 300 Fourier transform spectrometer at 300.13 MHz in CDCl$_3$ with tetramethylsilane (TMS) as internal standard.

The number-average molecular weight (M_n), weight-average molecular weight (M_w) and PDI of the samples were measured by gel permeation chromatography (GPC). Analyses were performed at 35 °C using THF (1.0 mL min^{-1}) as eluent, on a GPC-Max VE2001 GPC Solvent/Sample Module equipped with two columns: a universal column (T6000M, Org 300×7.8 mm) followed by a linear column (T4000, Org 300×7.8 mm), and two detectors: a refractometric index detector (RT VE3580) and a dual detector (Viscotek 270). Calibration was performed using polystyrene as standards.

Differential scanning calorimetry (DSC) was carried out using DSC 2010 and an empty aluminum pan as a reference, samples (about 10 mg) were measured in aluminum pans under an atmosphere of dry nitrogen, the temperature range was set from -100 to 50 °C, and the measurements were performed at an advancing heating rate of 10 °C min^{-1}.

Metathetic Degradation Procedures. In a typical experiment, metathetic degradation of SBR was carried out in a reactor equipped with a mechanical stirrer, placed inside a glove box under nitrogen atmosphere at 30 °C. 0.5 g SBR was
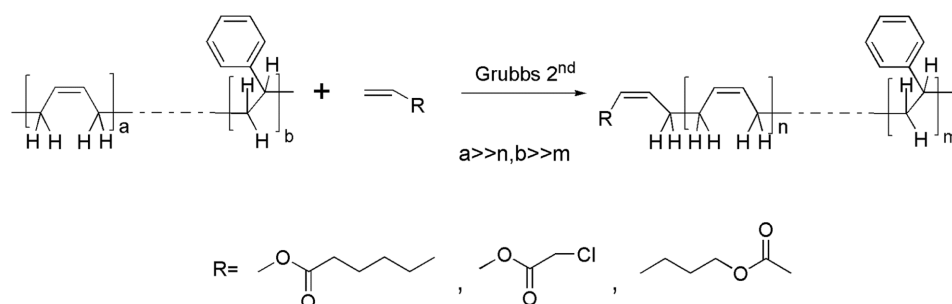
Scheme 1. Metathetic degradation and functionalization of SBR with different CTAs in the presence of G2.

Table 1. GPC Results of Products via Metathetic Degradation of SBR with Allyl Hexanoate

Entry	[-C=C-]:[Catalyst][b]	[-C=C-]:[CTA]	Time (h)	$M_n{}^c$ (g mol^{-1})	$M_w{}^c$ (g mol^{-1})	PDI^c
SBR^a				58900	288000	4.89
1	10000:1	2:1	2	23300	111500	4.79
2	8000:1	2:1	2	16800	35400	2.11
3	4000:1	2:1	2	1790	2600	1.45
4	2000:1	2:1	2	930	1240	1.33
5	1000:1	2:1	2	830	970	1.17
6	2000:1	10:1	2	1180	1670	1.42
7	2000:1	50:1	2	3000	6310	2.10

(solvent: 1, 2-dichloroethane; temperature: 30 °C; [-C=C-]=0.3 mol L^{-1})
^{a}SBR: styrene-butadiene rubber. ^{b}Molar ratio of [-C=C-]:[catalyst]. ^{c}Experimental number-average molecular weight (M_n), weight-average molecular weight (M_w) and PDI measured by gel permeation chromatography (GPC) calibrated with polystyrene standard; PDI: polydispersity index measured by GPC.

dissolved in 25 mL 1,2-dichloroethane in an oil bath. The CTA (5-hexenyl acetate, allyl hexanoate, allyl chloroacetate or trifluoroethyl methacrylate) was added to the stirred solution of SBR with various molar ratios of [-C=C-]:[CTA]=5:1, 10:1, 50:1, 100:1. The G2 catalyst was then introduced directly to the solution at different molar ratios of [-C=C-]:[catalyst]= 1000:1, 2000:1, 4000:1, 8000:1, 10000:1. Aliquots of the reaction mixture were sampled at different reaction time, and the reaction was terminated by adding an excess amount of methanol and exposed to air. The reaction solution was then concentrated under vacuum at 50 °C and the residue was carefully dissolved in 1,2-dichloroethane (minimum volume) and precipitated in excess methanol to obtain the telechelic oligomers.

Results and Discussion

The reaction mechanism for metathetic degradation and functionalization of SBR with different CTAs in the presence of G2 is illustrated in Scheme 1. Investigations were made to show that an important molecular weight reduction took place after the metathetic degradation with the addition of 5-hexenyl acetate, allyl hexanoate, allyl chloroacetate or trifluoroethyl methacrylate.

Allyl Hexanoate as a Chain Transfer Agent. Cross-metathesis reactions of the SBR were performed in 1, 2-dichloroethane using the G2 catalyst and allyl hexanoate. The effects of the catalyst quantity and CTA quantity on the M_n and PDI of the products were investigated and the experimental results calculated from GPC are depicted in Table 1. The molar ratio of [-C=C-]:[CTA] was fixed at 2:1 and the reaction time was set to 2 h. When the molar ratio of [-C=C-]:[catalyst]=10000:1 was used, the M_n of the oligomers decreased to 23300 from 58900 g mol^{-1}. When the molar ratio was changed to 1000:1, SBR oligomers with very low M_n and PDI (M_n=830 g mol^{-1} and PDI=1.17) were obtained. Based on these results, it could be concluded that the M_n and PDI of obtained metathesis products could be tuned on a large scale by changing the molar ratios of [-C=C-]:[catalyst] from 10000:1 to 1000:1. And the G2 catalyst was an efficient cross-metathesis catalyst with SBR as the substrate. Molar ratios of [-C=C-]:[CTA] ranging from 50:1 to 2:1 were investigated (entries 4, 6, 7 in Table 1). The M_n of the products was decreased from 3007 to 930 g mol^{-1}
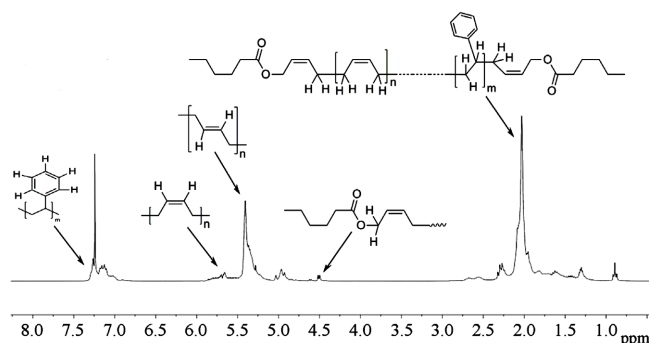
Figure 1. ^{1}H NMR spectrum of oligomers obtained via metathetic degradation of SBR with allyl hexanoate (entry 4 in Table 1).

Table 2. GPC Results of Products via Metathetic Degradation of SBR with Allyl Hexanoate

Entry	[-C=C-]: [Catalyst]	Time (h)	M_{n} (g mol^{-1})	M_{w} (g mol^{-1})	PDI
SBR			58900	288000	4.89
1	2000	1/12	12600	32400	2.57
2	2000	1/4	2460	5200	2.11
3	2000	1/2	1430	2380	1.66
4	2000	1	1170	1520	1.30
5	2000	2	930	1240	1.33
6	2000	4	840	1140	1.36
7	2000	8	720	920	1.28
8	2000	12	700	950	1.36

Solvent: 1,2-dichloroethane; temperature: 30 °C; [-C=C-]=0.3 mol L^{-1}; molar ratio of [-C=C-]:[CTA]=2:1.

Figure 2. GPC curves of oligomers obtained via degradation of SBR with allyl hexanoate (solvent: 1, 2-dichloroethane; temperature: 30 °C; molar ratio of [-C=C-]:[CTA]=2:1; molar ratio of [-C=C-]:[catalyst]=2000:1; reaction time (*t*): (a) *t*=5 min; (b) *t*=15 min; (c) *t*=1 h; (d) *t*=2 h; (e) *t*=12 h).
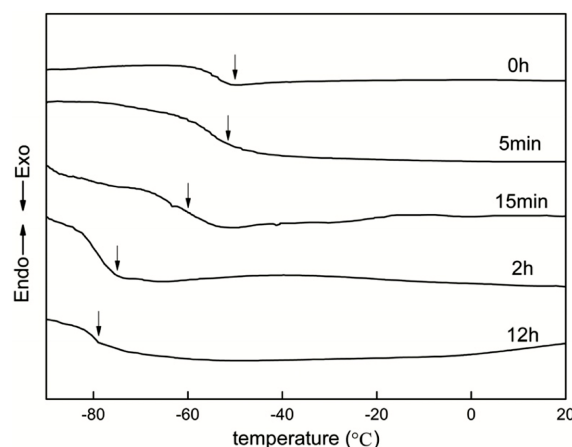
Figure 3. DSC thermograms of SBR oligomers obtained via degradation of SBR with allyl hexanoate.

when the reaction time was 2 h. The ^{1}H NMR spectrum of the obtained low M_{n} SBR telechelic oligomers (entry 4 in Table 1) depicted in Figure 1 shows evidence for the functionalization of SBR. The new signals observed at 4.50 and 4.52 ppm were assigned as the protons of hexanoate group attached to the polymer chain. Thus, allyl hexanoate was an excellent cross-metathesis partner for SBR.

In order to investigate the influence of the reaction time, experiments were carried out with durations from 5 min to 12 h. The results are summarized in Table 2. When the reaction reached 15 min, the M_{n} value had already decreased to 2460 g mol^{-1} at a quite fast degradation speed (entry 2 in Table 2). However, M_{n} was not observed to decrease rapidly in the next few hours (entries 3-7 in Table 2). When the reaction time was extended to 12 h, A M_{n} value of 700 g.mol^{-1}and lower polydispersity (1.36) was obtained, which indicated an identical well controlled metathesis degradation. Thus, we can conclude that
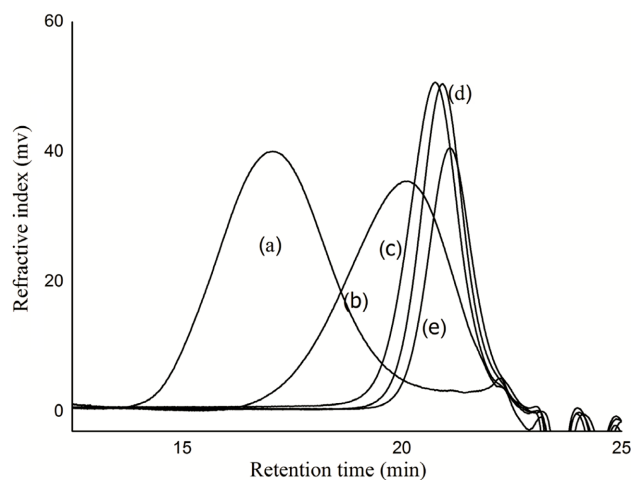
the increase of the degradation process is highly associated with the increase of the reaction time. GPC analysis (entry1-2, 4-5, 8 in Table 2 and Figure 2) shows the chromatograms shifting towards the right, which also confirms the shift of M_{n} towards lower values with longer reaction time.

The DSC technique was invited to measure the T_{g} for SBR oligomers. In the case of the initial SBR sample, the T_{g} was observed at -53.34 °C (0 h). After 5 min, the M_{n} value dropped from 58900 to 12600 g mol^{-1}. The T_{g} of the metathesis product decreased to -55.48 °C. As the reaction proceeded, the T_{g}s of the products gradually shifted towards lower temperatures. When the M_{n} value decreased to 700 g mol^{-1} after 12 h, the T_{g} was observed at -79.80 °C. As demonstrated above, the T_{g}

showed the dependence on M_n of metathesis product. It decreased as lower M_n and shorter length of the polymer chain of SBR telechelics existed (Figure 3).

Allyl Chloroacetate and 5-hexenyl Acetate as Chain Transfer Agents. For better M_n control of the SBR telechelic oligmers via degradation of SBR with functional monoolefins, allyl hexanoate was replaced by allyl chloroacetate. The influence of allyl chloroacetate concentration was studied and the experimental GPC results are depicted in Table 3. For a given G2 catalyst quantity, products with lower M_n were obtained by changing the [-C=C-]:[CTA] ratios from 100:1 to 5:1 (entries 4, 5, 12 in Table 3) at 5 min, which revealed that allyl chloroacetate is also an excellent cross-metathesis CTA for SBR. In addition, with a fixed CTA concentration, lower M_n and PDI values were obtained by increasing the amount of G2 catalyst (entries 1-3, 5 in Table 3). Thus, it was shown that oligomers with designed and controllable M_n and PDI values could be achieved by adjusting the CTA and G2 catalyst concentrations. We also studied the evolution of the products' M_n and PDI with the over time (entries 5-11 in Table 3). It can be seen that the M_n of SBR telechelic oligomers decreased much more quickly in the first 5 min compared to when allyl hexanonate was used as CTA. However, the reaction rate leveled off rapidly after, thus showing a very slow decrease of M_n, which might be accounted for by the thermodynamic equilibrium of the degradation system.[42]

We obtained DSC thermograms of SBR oligomers (entries 5, 7, 9, 11 in Table 3), and the results are showed in Figure 4(a).

Table 3. GPC Results of Products via Metathetic Degradation of SBR with Allyl Chloroacetate

Entry	[-C=C-]:[CTA]	[-C=C-]:[Catalyst]	Time (h)	M_n (g mol^{-1})	M_w (g mol^{-1})	PDI
SBR				58900	288000	4.89
1	50:1	10000	1/12	36600	119000	3.25
2	50:1	4000	1/12	17400	41000	2.36
3	50:1	1000	1/12	1950	3850	1.97
4	5:1	2000	1/12	1470	3550	2.41
5	50:1	2000	1/12	3830	6460	1.69
6	50:1	2000	1/4	1730	4260	2.46
7	50:1	2000	1/2	1530	3150	2.06
8	50:1	2000	1	1290	2650	2.05
9	50:1	2000	2	1120	1590	1.42
10	50:1	2000	8	1130	1680	1.49
11	50:1	2000	24	770	1060	1.38
12	100:1	2000	1/12	5420	9090	1.67

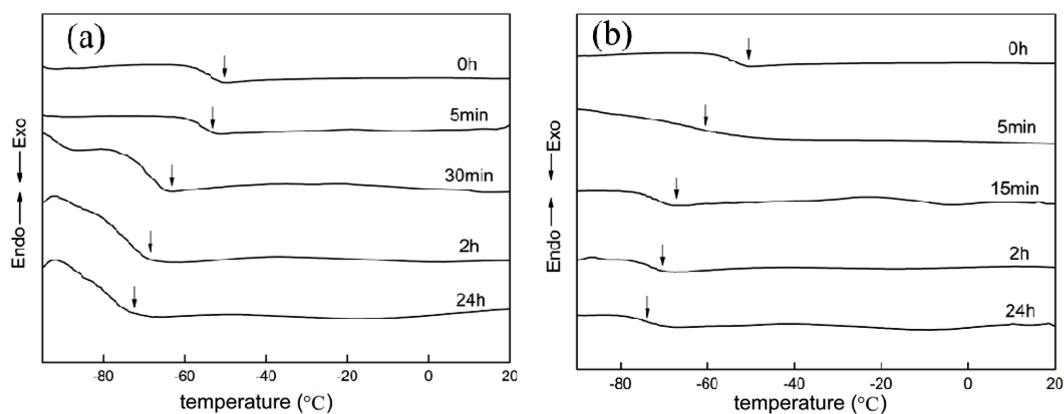Solvent: 1,2-dichloroethane; temperature: 30 °C; [-C=C-]=0.3 mol L^{-1}.

Figure 4. DSC thermograms of SBR oligomers obtained via degradation of SBR with different CTAs: (a) allyl chloroacetate; (b) 5-hexenyl acetate.

As the reaction proceeded, the glass transition temperatures of the products gradually shifted towards lower temperatures. The T_gs for SBR oligomers obtained at different reaction time (5, 30 min, 2, 24 h) were observed at -57.39, -68.38, -73.48 and -78.71 °C, respectively. The T_g also showed the dependenc on M_n of metathesis product. It decreased as lower M_n (from 58900 to 770 g mol^{-1}) and shorter length of the polymer chain of SBR telechelics existed. Thus it confirmed that the synthesis of highly degraded and functionalized SBR oligomers with specific CTA and the G2 catalyst were achieved in the present system.

To further investigate the degradation and functionalization of SBR catalyzed by ruthenium complex, 5-hexenyl acetate was also introduced to control M_n of the metathesis products by changing the reaction variables. Experiments were performed under the same condition as allyl chloroacetate. The GPC results are summarized in Table 4. Molar ratios of [-C=C-]: [CTA] ranging from 10:1 to 100:1 were investigated (entries 3, 4, 10 in Table 4). The trend of changes in M_n and PDI was consistent with those of the products obtained via metathesis degradation of SBR with allyl hexanoate and allyl chloroacetate, which also revealed that 5-hexenyl acetate was a highly effective CTA for the metathetic degradation of SBR. Reactions with molar ratios of [-C=C-]:[catalyst] from 10000:1 to 2000:1 were also studied (entries 1, 2, 4 in Table 4). The M_n value dropped from 58900 to 5130 g mol^{-1} after 5 min when the molar ratio of [-C=C-]:[catalyst] was 10000:1, and when the molar ratio of [-C=C-]:[catalyst] was changed to 2000:1, the M_n decreased to 2660 g mol^{-1}. Additionally, based on the M_n and PDI values of products at different reaction time (entries 4-
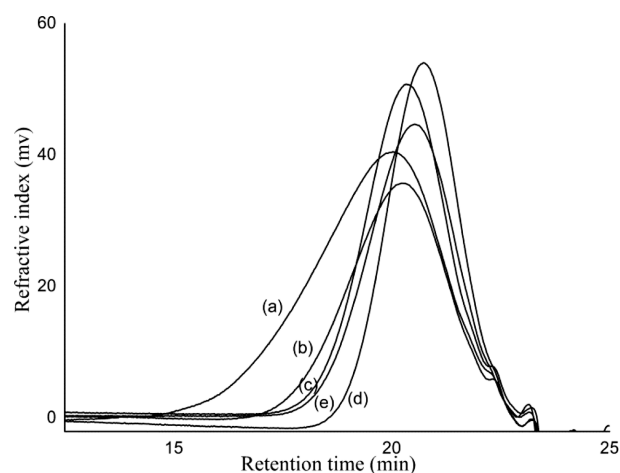

Figure 5. GPC curves of oligomers obtained via degradation of SBR with 5-hexenyl acetate (solvent: 1, 2-dichloroethane; temperature: 30 °C; molar ratio of [-C=C-]:[CTA]=50:1; molar ratio of [-C=C-]:[catalyst]=2000:1; reaction time (t): (a) t=5 min; (b) t=15 min; (c) t=1 h; (d) t=2 h; (e) t=24 h).

9 in Table 4), it can be concluded that similar to the situation of allyl chloroacetate, the reaction proceeded quite fast in the first 5 min and reached its equilibrium within 2 h. The M_n of the oligomers showed no considerable differences when the reaction time was extended to 24 h. Figure 5 shows the shift of the chromatograms towards a low M_n when the reaction time was extended. Thus, the degree of metathetic degradation could be controlled by adjusting the reaction time, CTA concentration and G2 concentration.

We also obtained DSC thermograms of SBR oligomers (entries 4, 5, 7, 9 in Table 4), and the results are showed in Figure 4(b). As expected, the glass transition temperatures of the

Table 4. GPC Results of Products via Metathetic Degradation of SBR with 5-Hexenyl Acetate

Entry	[-C=C-]:[CTA]	[-C=C-]:[Catalyst]	Time (h)	M_n (g mol^{-1})	M_w (g mol^{-1})	PDI
SBR				58900	288000	4.89
1	50:1	10000:1	1/12	5130	10300	2.00
2	50:1	4000:1	1/12	4430	9410	2.12
3	10:1	2000:1	1/12	1440	2950	2.05
4	50:1	2000:1	1/12	2660	5560	2.09
5	50:1	2000:1	1/4	1380	3250	2.36
6	50:1	2000:1	1	1250	2700	2.16
7	50:1	2000:1	2	970	1660	1.71
8	50:1	2000:1	8	940	1430	1.52
9	50:1	2000:1	24	1030	2340	2.27
10	100:1	2000:1	1/12	5870	15120	2.58

Solvent: 1,2-dichloroethane; temperature: 30 °C; [-C=C-]=0.3 mol L^{-1}.
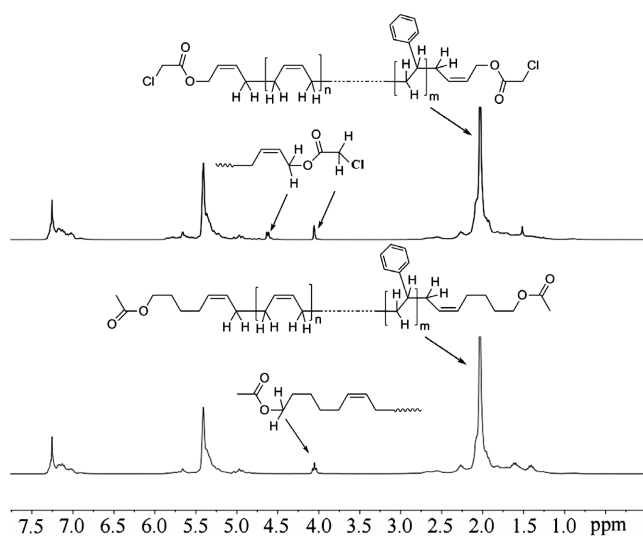
Figure 6. ^{1}H NMR spectra of oligomers obtained via metathetic degradation of SBR with allyl chloroacetate (entry 11 in Table 3, above) and 5-hexenyl acetate (entry 9 in Table 4, below).

products gradually shifted towards lower temperatures. The T_gs for SBR oligomers obtained at different reaction time (5, 15 min, 2, 24 h) were observed at -59.71, -66.07, -70.12 and -74.48 °C, respectively. The T_g decreased as M_n value decreased from 58900 to 1030 g mol^{-1}.

Figure 6 unambiguously illustrates the ^{1}H NMR spectra of end-functionalized telechelic oligomers obtained via cross-metathesis of SBR with allyl chloroacetate (entry 11 in Table 3) and 5-hexenyl acetate (entry 9 in Table 4). The newly appearing signals confirmed the formation of end function-alized SBR oligomers.

Trifluoroethyl Methacrylate as a Chain Transfer Agent. To probe into the SBR degradation and functionalization process further, fluoro-substituted olefin like trifluoroethyl meth-acrylate was used as CTA. The influences of CTA concentration and reaction time were also studied. The GPC data of SBR oligomers are summarized in Table 5. Unexpectedly, the molecular weight values of SBR oligomers were relatively high and changed irregularly with the molar ratios of [-C=C-]:

[CTA] ranging from 2:1 to 100:1 at 2 h (entries 1, 2, 4 in Table 5). When prolonging the reaction time, the GPC analysis demonstrated little M_n variation (entry 3 in Table 5). In addition, the analysis of ^{1}H NMR showed no new peak appearing, which demonstrated that the functional group of the fluori-nated alkene was not successfully attached to the SBR polymer chain. The failure of the metathesis could be explained by a low efficacy of the catalyst towards this highly functionalized monomer for the degradation and functionalization of SBR.

Conclusions

The success of metathetic degradation and functionalization of SBR with different CTAs in the presence of the G2 catalyst has been demonstrated. Different molar ratios of [-C=C-]: [CTA] and [-C=C-]:[catalyst], as well as variations in reaction time were investigated. Well-defined telechelics with designed molecular weights in the range of 700-36600 and specific PDI values were obtained in a controllable manner. ^{1}H NMR and DSC analyses further confirmed the structures and properties of end-functionalized oligomers. Thus, allyl hexanoate, allyl chloroacetate and 5-hexenyl acetate functionalized as CTAs were excellent cross-metathesis partners for SBR. Neverthe-less, fluoro-substituted olefin like trifluoroethyl methacrylate was difficult to attach to the polymer chain of SBR compared with other CTAs, which elucidated trifluoroethyl methacrylate as a poor cross-metathesis partner for the metathesis degra-dation of SBR and it showed low activity towards the Grubbs catalyst. Further experiments are in progress to design and pro-duce various highly functionalized SBR telechelic oligomers.

Table 5. GPC Results of Products via Metathetic Degradation of SBR with Trifluoroethyl Methacrylate

Entry	[-C=C-]:[CTA]	[-C=C-]:[Catalyst]	Time (h)	M_n (g mol^{-1})	M_w (g mol^{-1})	PDI
SBR				58900	288000	4.89
1	100:1	2000:1	2	1470	6600	4.49
2	4:1	2000:1	2	2300	5120	2.23
3	4:1	2000:1	12	1970	4400	2.23
4	2:1	2000:1	2	1620	4980	3.07

Solvent: 1,2-dichloroethane; temperature: 30 °C; [-C=C-]=0.3 mol/L.

References

1. G. Natta, P. Pino, P. Corradini, F. Danusso, E. Mantica, G. Mazzanti, and G. Moraglio, *J. Am. Chem. Soc.*, **77**, 1708 (1955).
2. G. Natta, *J. Polym. Sci.*, **16**, 143 (1955).
3. Y. Chauvin, *Angew. Chem. Int. Ed.*, **45**, 3740 (2006).
4. F. N. Tebbe, G. W. Parshall, and D. W. Ovenall, *J. Am. Chem. Soc.*, **101**, 5074 (1979).
5. L. R. Gilliom and R. H. Grubbs, *Organometallics*, **5**, 721 (1986).
6. L. R. Gilliom and R. H. Grubbs, *J. Am. Chem. Soc.*, **108**, 733 (1986).
7. M. Leconte and J. M. Basset, *J. Am. Chem. Soc.*, **101**, 7296 (1979).
8. R. R. Schrock, R. T. Depue, J. Feldman, K. B. Yap, D. C. Yang, W. M. Davis, L. Park, M. Dimare, M. Schofield, J. Anhaus, E. Walborsky, E. Evitt, C. Kruger, and P. Betz, *Organometallics*, **9**, 2262 (1990).
9. G. C. Bazan, R. R. Schrock, and M. B. Oregan, *Organometallics*, **10**, 1062 (1991).
10. R. R. Schrock and A. H. Hoveyda, *Angew. Chem. Int. Ed.*, **42**, 4592 (2003).
11. R. R. Schrock, *Tetrahedron*, **55**, 8141 (1999).
12. T. M. Trnka and R. H. Grubbs, *Acc. Chem. Res.*, **34**, 18 (2001).
13. R. H. Grubbs, *Angew. Chem. Int. Ed.*, **45**, 3760 (2006).
14. M. S. Sanford, J. A. Love, and R. H. Grubbs, *J. Am. Chem. Soc.*, **123**, 6543 (2001).
15. D. Reyx and I. N. Campistron, *Angew. Makromol. Chem.*, **247**, 197 (1997).
16. T. Morita, B. R. Maughon, and R. H. Grubbs, *Polym. Chem.*, **215**, 414 (1998).
17. K. J. Ivin and J. C. Mol, *Olefin Metathesis and Metathesis Polymerization*, Academic Press, London, 1997.
18. M. Lazar and J. Rychly, *Adv. Polym. Sci.*, **102**, 189 (1992).
19. G. Scott, *Polym. Degrad. Stabil.*, **48**, 315 (1995).
20. V. G. Dedgaonkar, P. B. Navle, and P. G. Shrotri, *Radiat. Phys. Chem.*, **48**, 333 (1996).
21. W. Ast and K. Hummel, *Naturwissenschaften*, **57**, 545 (1970).
22. K. Hummel, *Pure Appl. Chem.*, **54**, 351 (1982).
23. K. Hummel, R. Chemelli, H. Griesser, V. N. G. Kumar, and F. Stelzer, *Makromol. Chem. Rapid Commun.*, **4**, 429 (1983).
24. K. Hummel, *J. Mol. Catal.*, **28**, 381 (1985).
25. K. Hummel, H. Lechner, H. Zekoll, and R. Chemelli, *Makromol. Chem.-Macromol. Chem. Phys.*, **188**, 1075 (1987).
26. K. Hummel and A. Paschen, *Polym. Bull.*, **24**, 391 (1990).
27. E. Hubmann, K. Hummel, M. Dosinger, T. Pongratz, and R. Saf, *Makromol. Chem.-Macromol. Chem. Phys.*, **191**, 1799 (1990).
28. K. Hummel, E. Hubmann, M. Dosinger, and T. Pongratz, *Eur. Polym. J.*, **27**, 303 (1991).
29. K. Hummel, N. Kiattanavith, K. Martl, and C. Mirtl, *J. Mol. Catal.*, **76**, 239 (1992).
30. J. C. Marmo and K. B. Wagener, *Macromolecules*, **26**, 2137 (1993).
31. J. C. Marmo and K. B. Wagener, *Macromolecules*, **28**, 2602 (1995).
32. S. K. Cummings, D. W. Smith, and K. B. Wagener, *Macromol. Rapid Commun.*, **16**, 347 (1995).
33. M. D. Schulz, R. R. Ford, and K. B. Wagener, *Polym. Chem.*, **4**, 3656 (2013).
34. T. R. Younkin, E. F. Conner, J. I. Henderson, S. K. Friedrich, R. H. Grubbs, and D. A. Bansleben, *Science*, **287**, 460 (2000).
35. O. Brummer, A. Ruckert, and S. Blechert, *Chem. Eur. J.*, **3**, 441 (1997).
36. S. Gutierrez and M. A. Tlenkopatchev, *Polym. Bull.*, **66**, 1029 (2011).
37. S. S. Solanky, I. N. Campistron, A. Laguerre, and J. F. Pilard, *Macromol. Chem. Phys.*, **206**, 1057 (2005).
38. M. A. Tlenkopatchev, A. Barcenas, and S. Fomine, *Macromol. Theory. Simul.*, **10**, 441 (2001).
39. A. Acevedo, S. Fomine, S. Gutierrez, and M. A. Tlenkopatchev, *J. Organomet. Chem.*, **765**, 17 (2014).
40. A. Martinez, S. Gutierrez, and M. A. Tlenkopatchev, *Molecules*, **17**, 6001 (2012).
41. F. Sadaka, I. N. Campistron, A. Laguerre, and J. F. Pilard, *Polym. Degrad. Stabil.*, **98**, 736 (2013).
42. F. Lucas, F. Peruch, S. Carlotti, A. Deffieux, A. Leblanc, and C. Boisson, *Polymer*, **49**, 4935 (2008).