1494 *Macromolecules* **2000,** *33,* 1494−1496

Solvent-Free Olefin Metathesis Depolymerization of 1,4-Polybutadiene

Mark D. Watson and Kenneth B. Wagener*

George and Josephine Butler Polymer Research Laboratory, Department of Chemistry, University of Florida, Gainesville, Florida 32611-7200

Received September 14, 1999
Revised Manuscript Received December 30, 1999

Incorporation of unsaturated elastomers as substrates in olefin metathesis schemes has been investigated for 30 years, with applications including molecular weight modification, microstructure elucidation via conversion to small molecules more amenable to characterization, and the preparation of end-functionalized polymers.[1] These reactions also have implications in the recycling of commercial elastomers to chemical feedstocks.[2] In all previously reported cases, the reaction between solid polymers and metathesis catalysts has required a solvent to bring the two in contact on a molecular scale. In this paper, we report for the first time that the well-defined ruthenium catalyst, $Cl_2(Cy_3P)_2RuCHPh$ (**1**),[3] effects the clean metathesis depolymerization of high molecular weight 1,4-polybutadiene at room temperature; no solvent or any other added chain limiter is required. Further, we report on a phenomenon that we term “intramolecular chain limitation”.

The polymers used in this study were a *cis*-1,4-polybutadiene (**2**) possessing less than 1% 1,2-repeat unit content (Aldrich #18,137-4; 98% *cis*-1,4; MW = $(2-3) \times 10^6$ g/mol) and a similar 1,4-polybutadiene (**3**) possessing a 9% 1,2-repeat unit content (Aldrich #18,138-2; 36% cis, 55% trans, 9% 1,2; MW = 4.2×10^5 g/mol).[4] As a first example, solid ruthenium catalyst **1** was simply sprinkled on the surface of particles of the high molecular weight polymer at room temperature using 0.25 mol % of catalyst in an inert atmosphere. Within an hour the surface of the polymer began to visually liquefy, eventually leading to a homogeneous viscous liquid within 2−3 h with the aid of mechanical agitation. After 48 h, the ^1H and ^{13}C NMR spectra were consistent with 1,4-polybutadiene (72% trans content by quantitative ^{13}C NMR), but analysis by GPC revealed a molecular weight decrease of 2 orders of magnitude ($\bar{M}_n = 7.2 \times 10^3$ g/mol, PDI = 2.0, vs polystyrene). The fact that the trans/cis ratio of the resultant polymer approaches the typical 80/20 for the metathesis of internal olefins, along with the generation of a most probable polydispersity ratio, indicates that depolymerization equilibrium has been reached.

Prior work by us[5] and others as well[1] has shown that depolymerization of high molecular weight unsaturated polymers via metathesis in dilute solution leads primarily to ring structures or under more concentrated conditions to telechelic oligomers when external monoene chain limiters are present. The experiments reported herein illustrate that added chain limiters *are not needed* to produce lower molecular weight linear polymers when the reaction is carried out in bulk. Further, while the catalyst may initially act as the chain limiter (Figure 1), the equilibrium molecular weight generated for the polymer is the result of trace 1,2-butadiene linkages participating in chain limitation (Figure 2).

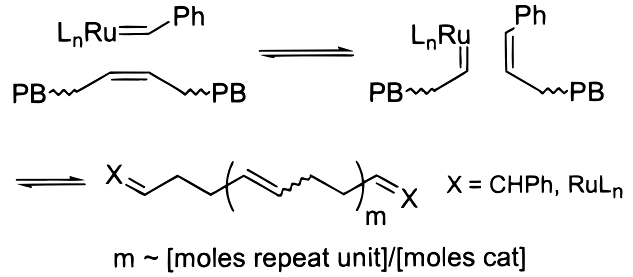

Figure 1. Molecular weight reduction via incorporation of catalyst residues as chain limiters.

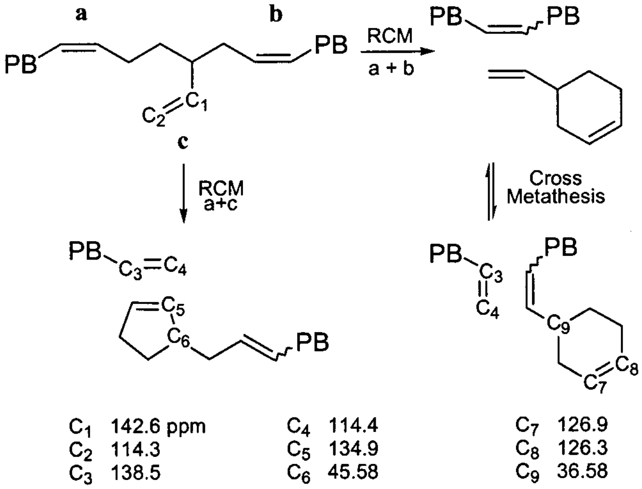

Figure 2. Molecular weight reduction via conversion of 1,4−1,2−1,4 triads to chain limiters. Selected carbons numbered for identification by ^{13}C NMR (vide infra).

cis-1,4-Polybutadiene (**2**) is well above its crystalline melting point and glass transition temperature (T_m = −6 °C, T_g = −102 °C)[6] at room tempeature, so adequate translational, rotational, and vibrational energies exist to permit the metathesis reaction of catalyst **1** with the internal olefin sites of the polymer; the molecular motion in the polymer is sufficient to imbibe the catalyst forming a “solution” at the interface. Thus, upon initiation of the reaction, the polymer itself becomes the “solvent”, and equilibrium conversion leading to depolymerization becomes entropically driven. In the absence of added external chain limiters (monoenes) the position of this depolymerization equilibrium is dictated by three contributing metathesis processes: (a) conversion of polymer to cyclics, (b) incorporation of the catalyst **1** within the polymer as a chain limiter, and (c) conversion of 1,4−1,2−1,4 triads as chain limiters, a phenomenon we call intramolecular chain limitation.

Figure 1 illustrates how the catalyst can act to decrease chain length. The ruthenium catalyst reacts with the olefinic backbone resulting in chain scission, producing two new chains with β-styryl and ruthenium carbene termini. The reactive ruthenium carbene may then migrate from chain to chain producing two new chains with altered molecular weight with each metathesis step, eventually approaching the most probable distribution (PDI = 2) of linear chains terminated by the catalyst residues.

If the catalyst alone was the sole source of chain limitation, then the average molecular weight would be

10.1021/ma991560p CCC: $19.00

proportional to the repeat unit-to-catalyst ratio as is the case in any living polymerization. However, when the experiment was repeated decreasing the catalyst concentration from 0.25 to 0.025 mol %, the depolymerization equilibrium product had essentially the same molecular weight. This means another source of chain limiter must be present, and the alternate source is, in fact, the 1,2-repeat units present within all commercial 1,4-polybutadienes (Figure 2).

Even nearly perfect, commercial grade *cis*-1,4-polybutadiene may contain up to 0.5% 1,2-repeat units.[7] The presence of these linkages in polymer **1** is revealed in the ^{1}H NMR as a diminutive multiplet at approximately 4.9 ppm (vinyl CH_2 protons). Further, it has been shown[8] that the spacial placement of double bonds in 1,4−1,2−1,4 triads favors formation of cyclopentene and cyclohexene derivatives via ring-closing metathesis (RCM), an observation pertinent to these 1,2-repeat units acting as chain limiters. This possibility is also substantiated by Grubbs' observation that the exposure of high molecular weight 1,2-polybutadiene to metathesis catalysis results in molecular weight reduction and that the decrease is related to the concentration of trace 1,2−1,4−1,2 triads.[9]

Consequently, and as shown in Figure 2, we propose that the 1,2-repeat units in 1,4−1,2−1,4 triads present in polymer **2** also serve as "intramolecular chain limiters" in the depolymerization chemistry via ring-closing metathesis. The RCM reaction along the backbone olefins (bonds a and b) of a 1,4−1,2−1,4 triad extrudes vinylcyclohexene with relatively infinitesimal decrease in chain size. This molecule then can act as a chain limiter via cross-metathesis of the vinyl group with the polymer backbone. Alternately, the RCM reaction of the vinyl group of the triad with an adjacent backbone olefin (bonds a and c) results in direct chain scission. The net result of both of these possibilities upon equilibration depolymerization is the formation of lower molecular weight 1,4-polybutadiene terminated by vinyl, cyclohexenyl, and cyclopentenyl groups with average molecular weight related to the mole percent 1,2-linkages. Provided that the catalyst loading is kept low, the molar ratio of catalyst is no longer a primary factor in determining average molecular weight of the depolymerization product, which is what we observe.

If the mole percent of 1,2-linkages in polymer **2** is estimated at 0.5%, the predicted degree of polymerization of entirely linear polymers produced in this fashion is 200 ($\bar{M}_n = 1.08 \times 10^3$), which is in reasonable agreement with the measured value. Evidence of the proposed cyclic end groups is found by a new, small unresolved multiplet at 5.64 ppm (^{1}H NMR), corresponding well with resonances of the ring olefinic protons of similarly substituted cyclohexenes and cyclopentenes (~5.7 ppm). Inclusion of the 0.25 or 0.025 mol % of catalyst **1** as additional end groups makes relatively little difference in the predicted degree of polymerization.

The above hypothesis was verified by depolymerizing a 1,4-polybutadiene sample possessing a higher concentration of 1,2-repeat units under identical reaction conditions; lower molecular weight depolymerization products were the result. The solid-state depolymerization of a commercially available 1,4-polybutadiene (**3**) containing 9% 1,2-repeat units (MW = 4.2×10^5) proceeded as before and yielded a 1,4-polybutadiene of $\bar{M}_n = 1.2 \times 10^3$ (PDI = 2.0). ^{13}C NMR signals of the starting polymer can be adequately assigned on the basis of the literature,[10] and new signals in the product mixture were tentatively assigned to the proposed end groups as shown in Figure 2. A DEPT NMR experiment reveals the presence of new methine carbons in the sp^2 region which are assigned to the ring olefinic carbons of the cyclopentenyl and cyclohexenyl groups. The signals corresponding to the vinyl carbons of 1,2-linkages are shifted to values corresponding to the vinyl end groups shown in Figure 2, which are identical to those of polybutadiene produced via ADMET polymerization of 1,5-hexadiene. Additionally, new methines were observed in the sp^3 region, which are diagnostic for the methine ring carbons of vinylcyclohexene and allylcyclopentene moieties. Finally, trace end groups may arise from the low concentration of triads containing more than one 1,2-linkage, but these were not observed.

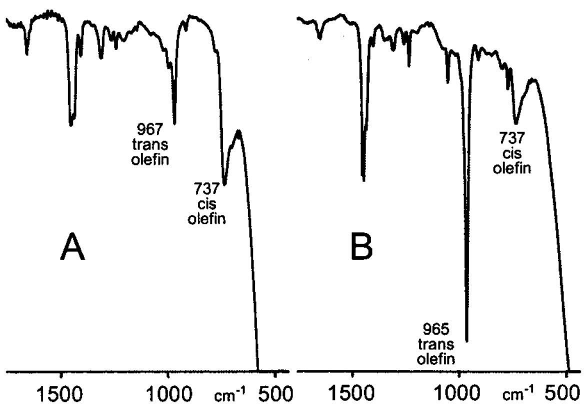

Figure 3. Partial IR spectra of polybutadiene **2** after 1 h exposure to catalysts **1** (A) and **4** (B).

Attempts[5d] to effect bulk equilibrium depolymerization of polymer **2** with the well-known complex $(R_FO)_2$-NArMo=CHCMe$_2$Ph (**C2**, Ar = 2,6-(iPr)$_2C_6H_3$, R_F = CMe(CF$_3$)$_2$)[11] (**4**) met with failure, which may seem puzzling in light of the greater reactivity and comparable solubility of this catalyst with alkyl olefins. Reexamination reveals the apparent ineffectiveness of catalyst **4** is not due to its inability to initiate metathesis chemistry but instead due to its greater propensity to form trans products in the early stages of reaction. When catalyst **4** is placed on the surface of polymer **2**, close visual inspection shows the surface begins to liquefy during the first 30 min but soon becomes waxy and friable with no apparent further reaction over 48 h. The surface layer was scraped from two separate samples after 1 h exposure to catalysts **1** and **4** without agitation, and these samples were examined by IR (Figure 3) and ^{13}C NMR (Figure 4). The spectra qualitatively show that a large disparity in stereochemistry of the two samples exists during the early stages of reaction. Use of the molybdenum catalyst **2** produces a much higher trans content giving rise to the friable physical appearance, a consequence of the more crystallizable trans segments. Depolymerization in the case of the molybdenum catalyst therefore is aborted due to hindered chain-to-chain migration associated with slower diffusion kinetics in a progressively more crystalline polymer matrix.[12] Further, although polymer **3** has a high trans content (55%) to begin with, equilibrium depolymerization is still successful with catalyst **1** due to the higher 1,2-content. More rapid chain scission should result from the greater availability of end groups,

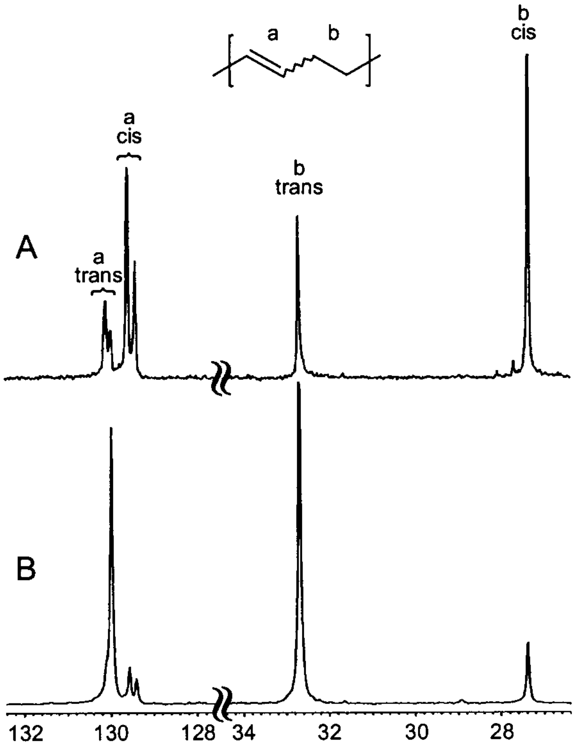

Figure 4. Partial ^{13}C NMR spectra of polymer **2** after 1 h exposure to catalyst **1** (A) and **2** (B).

which perhaps offsets any deleterious effect of higher initial trans content. These results show that successful bulk metathesis depolymerization hinges on the competition between equilibrium of cis/trans content versus statistical equilibration of chain lengths.

We conclude that the ruthenium catalyst **1** is the first observed to allow the solid-state depolymerization of an unsaturated polymer simply by mechanical mixing of the two compounds. After this observation, cross metathesis of polybutadiene with functionalized chain limiters in the bulk state becomes trivial,[13] leading to end-functionalized polymers of controlled molecular weight. Further, the role of the 1,2-repeat units in intramolecular chain limitation has been delineated. This depolymerization procedure clearly has merit in polymer recycling chemistry, and the method, followed by standard molecular weight measurements, may also constitute a facile semiquantitative measure of the 1,2-repeat unit content in polybutadiene.

Acknowledgment. We thank the National Science Foundation, Division of Materials Research, for their generous support of this research.

References and Notes

(1) Ivin, K. J.; Mol, J. C. *Olefin Metathesis and Metathesis Polymerization*; Academic Press: San Diego, 1997; Chapter 16.

(2) Wagener, K. B.; Wolfe, P. S.; Watson, M. D. In *Proceedings of the NATO Advanced Study Institue on Metathesis Polymerization of Olefins and Polymerization of Alkynes*; Imamoglu, Y., Ed.; Kluwer Academic Publishers: Dordrecht, 1998.

(3) Schwab, P. E.; France, M. B.; Ziller, J. W.; Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2039.

(4) Polymers were precipitated from toluene into MeOH, then degassed, and azeotropically dried under reduced pressure with sodium-dried toluene. All manipulations were conducted in an argon-purged drybox.

(5) (a) Wagener, K. B.; Marmo, J. C. *Macromolecules* **1993**, *26*, 2137. (b) Wagener, K. B.; Marmo, J. C. *Macromolecules* **1995**, *28*, 2602. (c) Marmo, J. C. ADMET Depolymerization: The Synthesis of Perfectly Difunctional Telechelics. Ph.D. Disseration, University of Florida, Gainesville, 1994. (d) Wagener, K. B.; Marmo, J. C. *Macromol. Rapid Commun.* **1995**, *16*, 557.

(6) Furuta, I.; Kimura, S.-I.; Iwama, M. In *Polymer Handbook*; Brandrup, J., Immergut, E. H., Grulke, E. A., Eds.; Wiley-Interscience: New York, 1999; pp V1−V2.

(7) Kaminsky, W. In *Handbook of Polymer Synthesis, Part A*; Kricheldorf, H. R., Ed.; Marcel-Dekker: New York, 1992; pp 389−391.

(8) (a) Abendroth, H.; Canji, E. *Makromol. Chem.* **1975**, *176*, 775. (b) Thorn-Csanyi, E.; Perner, H. *Makromol. Chem.* **1979**, *180*, 919.

(9) Coates, G. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 229.

(10) (a) Assignment of sp^3 carbons: Sato, H.; Takebayashi, K.; Tanaka, Y. *Macromolecules* **1987**, *20*, 2418. (b) Assignment of sp^2 carbons: van der Velden, G.; Didden, C.; Veermans, T.; Beulen, J. *Macromolecules* **1987**, *20*, 1252. Polymer **PB2** was included in the latter study.

(11) Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875.

(12) Vrentas, J. S.; Duda, J. L. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Kroschwitz, J. I., Ed.; Wiley-Interscience: New York, 1985; Vol. 15, pp 36−38. Successful depolymerization with catalyst **4** can be achieved simply by warming the semicrystalline product mixture.

(13) Chain limiter was prepared immediately prior to use by metathetical dimerization of ethyl 10-undecenoate. The chain limiter/catalyst residue mixture was added to polymer **2** and depolymerization conducted as above to yield ester-terminated polybutadienes with average molecular weight proportional to the molar ratio of chain limiter to repeat unit. Reaction between polymer **2** and ethylene, catalyzed by **1** in the bulk state, also successfully produces vinyl-terminated oligomers.

MA991560P