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Free Radical Carbonylation of 1,4-*cis*-Polybutadiene

C. Chatgilialoglu,*[,1] C. Ferreri,[1,2] and A. Sommazzi[3]

I.Co.C.E.A., Consiglio Nazionale delle Ricerche
Via P. Gobetti 101, 40129 Bologna, Italy
Istituto Guido Donegani, Via Fauser 4
28100 Novara, Italy

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The copolymerization of olefins with carbon monoxide has been studied extensively over the last four decades.[4] This reaction is used, on both industrial and laboratory scales, for the synthesis of polymeric materials containing ketonic groups. These polymeric materials are especially important due, at least, to the following reasons: (i) CO is particularly plentiful and inexpensive; (ii) the carbonyl chromophore renders these copolymers photodegradable; (iii) polyketones are useful starting materials for other types of functionalized polymers with specialized properties; (iv) some of them show high mechanical strength which results from a high crystallinity. In the early years the reactions were performed under free radical conditions in which peroxides, hydroperoxides, and azo compounds, as well as γ-rays, were widely used.[5] With the discovery that transition metals and their complexes catalyze the copolymerization of olefins with CO, the radical-initiated reactions were largely neglected.[6] The radical methodology produces *random* olefin−carbon monoxide copolymers (olefin:CO > 1),[7] whereas with the transition metal catalysts, a regular structure with *alternating* olefin and carbon monoxide units (olefin:CO = 1)[8] is obtained.

In the last decade, chemically modified polymers have gained increasing importance in the manufacture of rubbers and plastic materials. Unsaturated polymers are particularly suitable for such transformations. In a recent patent,[9] some of us described the free radical carbonylation of polydiene containing adjacent structural units derived from 1,4-*cis* polymerization of conjugated dienes. Polyketonic structures are also produced by this methodology. In fact, the new class of polymeric materials which results from the carbonylation contains randomly distributed repeating cycloketonic units along the chain. The origin of different ketonic moieties is the most intriguing aspect of this procedure, the mechanism of which also will be considered in this communication.

The modified polymers (**5**) were prepared by radical-initiated carbonylation of 1,4-*cis*-polybutadiene.[10] In particular, 1.3 L of a toluene solution containing 1−4 g of polybutadiene and the radical initiator was charged under a nitrogen stream in a 2 L AISI steel autoclave, equipped with mechanical stirring means. Carbon monoxide was then added at constant pressure during the reaction time (ca. 6 h). Experiments were performed at temperatures of 80 °C (initiator: AIBN), 90 °C (dibenzoyl peroxide), and 140 °C (di-*tert*-butyl peroxide) and carbon monoxide pressures of 60 and 100 atm. After normal workup, the polymeric material was characterized by IR, ^{13}C, and ^{1}H NMR spectroscopies and elemental analysis. An important feature of this polymer modification is that the content of carbonyl units[11] and the ratio of cyclopentanone/cyclohexanone depend strongly on the experimental conditions, i.e. CO pressure and reaction temperature.

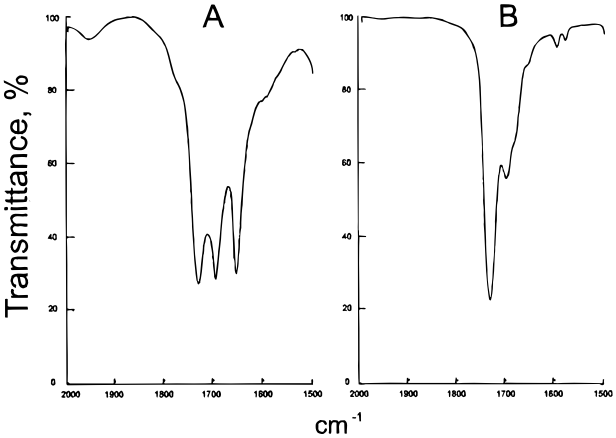

Figure 1. IR spectra of polymers A and B between 1500 and 2000 cm^{-1}, obtained using 60 and 100 atm of CO, respectively.

The IR spectra between 1500 and 2000 cm^{-1} of two samples are reported in Figure 1. Polymers A and B contain 5% and 20% CO by weight, respectively.[12] These products were obtained by using CO at 60 atm and AIBN or CO at 100 atm and dibenzoyl peroxide, respectively. The IR spectra of these polymers show characteristic carbonyl bands which are typical of cycloketone structures. Such bands are usually centered around the frequency of 1730 cm^{-1} for cyclopentanone units and 1700 cm^{-1} for cyclohexanone units. Ketonic structures, either from larger rings or from acyclic arrangements, display IR bands centered between 1650 and 1700 cm^{-1}.

In order to control both the incorporated amount of carbon monoxide and the ratio of cyclopentanone/cyclohexanone and, consequently, the properties of the resulting polymeric material,[13] mechanistic information regarding the elementary steps is needed.

The elementary steps that we conceived for the modification of 1,4-*cis*-polybutadiene are outlined in Scheme 1.[14] Radical **1**, initially generated by small amounts of the radical initiator, adds to carbon monoxide to form the acyl radical **2** that undergoes either a 5-*exo-trig* or a 6-*endo-trig* cyclization to form radicals **3** and **4**, respectively. Radical **4**, in turn, can either add to another CO molecule followed by a 6-*exo-trig* cyclization or undergo a 5-*exo-trig* cyclization to give carbonyl-containing

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[1] Consiglio Nazionale delle Ricerche.

[2] On sabbatical leave. Permanent address: Dipartimento di Chimica Organica e Biologica, Università di Napoli, Via Mezzocannone 16, 80134 Napoli, Italy.

[3] Istituto Guido Donegani.

[4] For reviews, see: (a) Sen, A. *Adv. Polym. Sci.* **1986**, *73/74*, 125. (b) Sen, A. *Acc. Chem. Res.* **1993**, *26*, 303.

[5] For the initial work, see: Brubaker, M. M. Coffman, D. D.; Hoehn, H. H. *J. Am. Chem. Soc.* **1952**, *74*, 1509.

[6] For recent work, see: (a) Sperrle, M.; Consiglio, G. *J. Am. Chem. Soc.* **1995**, *117*, 12130. (b) Jiang, Z.; Boyer, M. T.; Sen, A. *J. Am. Chem. Soc.* **1995**, *117*, 7037. (c) Jiang, Z.; Sen, A. *J. Am. Chem. Soc.* **1995**, *117*, 4455. (d) Forbes, M. D. E.; Ruberu, S. R.; Nachtigalliva, D.; Jordan, K. D.; Barborak, J. C. *J. Am. Chem. Soc.* **1995**, *117*, 3946.

[7] Polyketones with a low carbon monoxide content are currently used as photodegradable plastics. For example, see: (a) Bremer, W. P. *Polym. Plast. Technol. Eng.* **1982**, *18*, 137. (b) Leaversuch, R. *Mod. Plast. Int.* **1987**, *17*, 64.

[8] Drent, E.; Budzelaar, P. H. M. *Chem. Rev.* **1996**, *96*, 663.

[9] Sommazzi, A.; Cardi, N.; Garbassi, F.; Chatgilialoglu, C. U.S. Patent 5,369,187, 1994.

[10] The polybutadiene which has been used in this work contains 1,4-*cis* units of more than 98% and an average viscosimetric molecular weight of 200 000 as measured in toluene at 30 °C.

[11] CO content = [O$_2$ content (sample)] / 0.571. The O$_2$ content was determined by measuring the thermal conductivity of gases deriving from the pyrolysis of the sample. Therefore, the CO content is an indirect measurement of the amount of structural cycloketonic units.

[12] Although the IR spectra proved to be the most diagnostic, ^{13}C and ^{1}H NMR spectra also showed some important structural features, in particular at higher CO incorporation. The NMR spectra of polymer B are available in the supporting information.

[13] DSC analyses of the starting 1,4-*cis*-polybutadiene and the carbonylation products (polymers A and B) are the following (rate 20 °C/min): *polybutadiene* $T_g = -110$ °C, $T_c = -71$ °C, and $T_m = -8$ °C; *polymer A* $T_g = -108$ °C, $T_c = -60$ °C, and $T_m = -16$ °C; *polymer B* $T_g = -97$ °C, $T_c = 153$ °C, and $T_m \cong 300$ °C. It is evident that for the polymer with the higher incorporation of CO (20%), the thermal properties of the material change substantially. The thermograms are available in the supporting information.

[14] (a) Ryu, I; Sonoda, N.; Curran, D. P. *Chem. Rev.* **1996**, *96*, 177 and references cited therein. (b) Ryu, I.; Kusano, K.; Hasegawa, M.; Kambe, N.; Sonoda, N. *J. Chem. Soc., Chem Commun.* **1991**, 1018.

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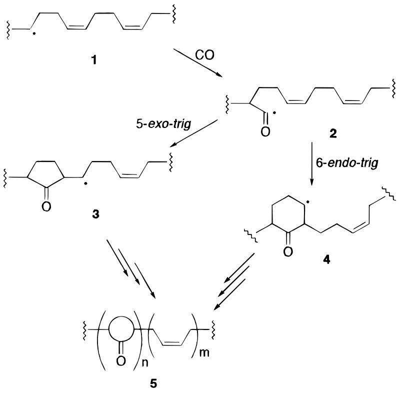
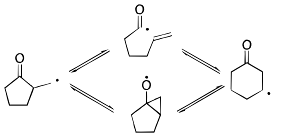
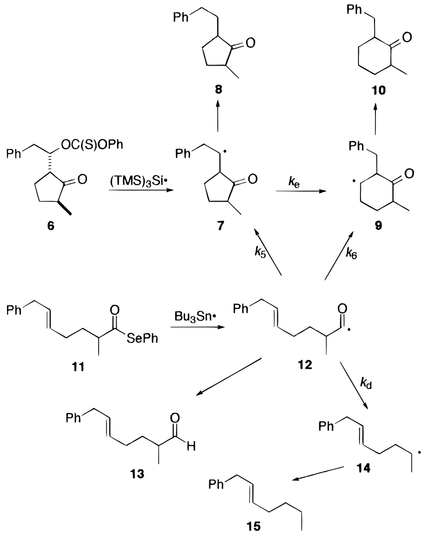
Scheme 1



Scheme 2



Scheme 3



bicyclic structures. Many repetitions of these elementary steps allow for the formation of polymer **5** which contains blocks of both cycloketonic groups and 1,4-*cis*-polybutadiene. As can be seen from Figure 1, an increase of the CO pressure leads to an increase in the cyclopentanone/cyclohexanone ratio. Therefore it is necessary to invoke a rearrangement of **3** to **4** in order to explain the ratio recovered in the experiments. A search of the literature[15] revealed the mechanistic picture illustrated in Scheme 2 for the cyclization of acyl radicals and the related one-carbon ring expansion. Since this overall mechanism is far from being understood, it brought us to design and perform the following model experiments.

To a degassed solution of either *erythro-trans* or *threo-trans* thionocarbonate **6**[16] (0.288 g; 0.80 mmol) and AIBN (0.013 g; 0.080 mmol) in benzene (5.5 mL), $(TMS)_3SiH$ (2.46 mL; 8.0 mmol) was added. The mixture was then heated at 80 °C for ca. 1 h until the starting thiocarbonate disappeared (TLC monitoring). GC analysis, using an internal standard, of the crude reaction mixture revealed the formation of cyclopentanone **8** (*trans* isomer) and cyclohexanones **10**[17] in a 6:1 ratio and quantitative yield. The mechanism for this reduction is outlined in Scheme 3. Tris(trimethylsilyl)silyl radicals remove the thionocarbonate moiety to form the secondary alkyl radical **7**.[16] This intermediate either abstracts a hydrogen atom from the silane to give **8** or rearranges to **9** followed by hydrogen transfer to afford **10**. The absence of compounds **13** and **15**[17] excludes the formation of the acyl radical **12** as an intermediate for the following reasons. The 1.0 M concentration of the silane remains essentially constant under our experimental conditions, and since the rate constant for the reaction of secondary alkyl radicals with $(TMS)_3SiH$ is 4.3×10^5 M^{-1} s^{-1} at 80 °C,[18] we estimate k_e (the rate constant for ring expansion) to be nearly 7×10^4 s^{-1} by applying free radical clock methodology.[19] From kinetic data[20] the rate constants for reactions **12** → **13** and **12** → **14** were calculated to be 7.2×10^4 M^{-1} s^{-1} and 3.7×10^5 s^{-1}, respectively, at 80 °C. Therefore, if the acyl radical **12** were an intermediate in the ring expansion, the rate constant for reaction **12** → **9** would have to be larger than 10^7 s^{-1} at 80 °C.

In order to measure the rate of the reaction **12** → **9**, we performed the following experiment. To a carefully degassed solution of phenylseleno ester **11** (0.200 g; 0.56 mmol) and AIBN (0.009 g; 0.056 mmol) in benzene (1.05 mL), tributyltin hydride (0.75 mL; 2.8 mmol) was added. The mixture was then heated at 80 °C for ca. 1 h until the starting thiocarbonate disappeared (TLC monitoring). GC analysis, using an internal standard, of the crude reaction mixture gave cyclopentanone **8** (yield 47%) and cyclohexanone **10** (6%) together with the aldehyde **13** (36%) and the alkene **15** (11%). The reactions expected to take place upon treatment of phenylseleno ester **11** with Bu_3SnH are also shown in Scheme 3. The acyl radical **12**, generated by the reaction of stannyl radical with phenylseleno ester **11**, disappeared following four independent paths: (i) hydrogen abstraction from the Bu_3SnH to give **13**; (ii) decarbonylation to give **14**; (iii) 5-*exo*-*trig* cyclization to give **7**; and (iv) 6-*endo*-*trig* cyclization to give **9**. At the high concentration of Bu_3SnH used in the experiment above, the rate constant for the path **7** → **8** is at least 50 times faster than k_e. Taking 3.7×10^5 s^{-1} as the rate constant for the decarbonylation (k_d) at 80 °C,[20] we calculated the rate constants for the 5-*exo*- and 6-*endo*-cyclizations (i.e. k_5 and k_6) to be 2×10^6 and 2×10^5 s^{-1}, respectively.

In conclusion, the radical-based reaction of 1,4-*cis*-polybutadiene with carbon monoxide afforded a new polymer containing repeating cycloketonic units. The model studies we performed prove that the formation of the six-membered ring is due either to direct cyclization of the acyl radical intermediate ($k_6 = 2 \times 10^5$ s^{-1}) or to the ring expansion ($k_e = 7 \times 10^4$ s^{-1}) of the previously formed five-membered ring ($k_5 = 2 \times 10^6$ s^{-1}). By taking into account the mechanistic information obtained for the elementary steps of this transformation, it is possible to perform the reaction with control of the incorporated amount of carbon monoxide and the ratio of cyclopentanone/cyclohexanone which, consequently, will be reflected in the properties of the resulting polymer.

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Supporting Information Available: Experimental procedures and compound characterization data (14 pages). See any current masthead page for ordering and Internet access instructions.

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(16) The diastereoisomerism is expected to be lost in the formation of the corresponding carbon-centered radical.

(17) In comparison with the retention time of their authentic samples.

(18) Chatgilialoglu, C.; Dickhaut, J.; Giese, B. *J. Org. Chem.* **1991**, *56*, 6399.

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