Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2016, **26**, 127–128

Mendeleev
Communications

Improved synthesis of polycarbynes

Tamara M. Zvukova,* Aleksandr I. Sizov and Boris M. Bulychev

Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation.
Fax: +7 495 932 8846; e-mail: tmzvukova@yandex.ru

DOI: 10.1016/j.mencom.2016.03.014

Two polymers of the polycarbyne family, namely poly(hydridocarbyne) and poly(phenylcarbyne), were synthesized by the magnesium-assisted reductive condensation of organic gem-trihalides in the presence of transition metal salts under mechanical activation.

$$\mathrm{CRHal_3 + Mg \xrightarrow[-\,MgHal_2]{\text{THF, cat., mechanical activation}} (CR)_{\mathit{n}}}$$

R = H, Ph
Hal = Cl, Br

Polycarbyne-family polymers, which are interesting owing to their unique capability to readily form the diamond structure upon heating, are still poorly available compounds. This prompts researchers to seek new methods of their synthesis. Earlier, we demonstrated[1] that poly(hydridocarbyne) **1** can be obtained by reacting $CHBr_3$ with magnesium metal in a mechanical activator (Scheme 1).

$$\mathrm{2\,CHBr_3 + 3\,Mg \xrightarrow[-\,3\,MgBr_2]{\text{THF, mechanical activation}} \underset{\mathbf{1}}{(CH)_{\mathit{n}}}}$$

Scheme 1

We discovered that the outcome of this reaction depends significantly on the activator surface material with which the reaction mixture is in contact. With an activator whose balls and jar inner surface are coated with a ceramic or plastic material, the yield of polymer **1** is considerably lower than the yields typically observed when the reaction mixture is in contact with uncoated steel surfaces. This fact led us to suppose that the observed difference is due to the catalytic action of iron derivatives that exist in the reaction mixture as a result of the abrasion of steel elements of the activator. The addition of salts of Fe, Cu, and Co (and other metals capable of being in two valence states) is known to alter the mechanism of carbon–carbon bond formation in the presence of organomagnesium compounds, *e.g.* the Wurtz–Grignard reaction gives way to the Kharasch reaction.[2] In view of this, we hypothesized that the addition of a transition metal salt would affect the reaction in our case as well. It was found later that addition of catalytic amounts of $FeCl_2$, $CuBr_2$, or $CoBr_2$ ensures a high yield of polymer **1** in all activators, including those with ceramic or plastic surfaces. The addition of $CoBr_2$ increased the yield of polymer **1** from 70 to 85%.[†]

Note that the catalyst exerts a marked effect on the molecular weight of the resulting polymer. Under our standard experimental conditions, reaction (see Scheme 1) carried out in the absence of $CoBr_2$ yields polymer **1** with an average molecular weight of about 3000, while reaction conducted in the presence of $CoBr_2$ yields polymer **1** with a lower molecular weight of 1500. It is noteworthy that the above molecular weight values characterize only the part of the polymer than can be isolated by reprecipitation from chloroform or THF. However, the products always contain not only the soluble fraction of polymer but also its

---

[†] Syntheses were carried out using magnesium as 2–3 mm chips. THF was purified by boiling over sodium under argon followed by distillation. $CHBr_3$ and $PhCCl_3$ were dried over $CaCl_2$ and distilled *in vacuo* immediately before use. ^{1}H NMR spectra were recorded on a Bruker DPX 300 spectrometer; IR spectra, on a Nicolet IR200 spectrometer; EPR spectra, on a Varian E 13 spectrometer at 20 °C. The molecular weight distribution and average molecular weight of the polymers were determined by gel permeation chromatography on a Waters chromatograph using THF as the eluent.

The activator was an AGO-2U high-speed centrifugal ball mill with water-cooled jars. The jars, ~100 cm^3 in volume, were made from steel. They were hermetically sealable and could be lined with a ceramic or plastic material. The balls (4–6 mm) were made from steel or ceramics.

The synthesis was carried out using an uncoated steel jar and steel balls for the reason that proper thermal contact between the reaction mixture and the metallic surfaces of the activator would ensure intensive heat removal and would allow the necessary reaction temperature to be maintained by means of external water cooling of the jars.

Synthesis of poly(hydridocarbyne) **1**. *Method A.* A jar of the AGO-2U activator, with balls inside, was heated to 130–150 °C and transferred into a dry nitrogen-filled glovebox, where it was allowed to cool to room temperature. Thereafter, the jar was charged with $CHBr_3$ (3.05 g, 12.1 mmol), magnesium (0.52 g, 21.6 mmol), $CoBr_2$ (50 mg), and THF (40 ml). Next, the jar was sealed and placed in the activator and the reaction was conducted for 3 min at a rotational speed of 890 rpm and a cooling water temperature of 15 °C. The reaction mixture was separated from the excess magnesium by decantation, 20 ml of ice-cold water was added, and the solvent was evaporated *in vacuo*. Water (50 ml) and concentrated HCl (1 ml) were added to the wet residue, and the mixture was subjected to extraction with $CHCl_3$ (80 ml) in a separatory funnel. The organic layer was separated from the aqueous layer, washed with distilled water (2×50 ml), and evaporated to dryness. The residue was vacuum-dried at 1×10^{-3} Torr and 40–45 °C for 3 h. The product was purified by dissolving it in CH_2Cl_2 (10 ml) followed by precipitation with hexane (50 ml) to obtain a brown powder (0.13 g, 85% yield). IR (KBr, ν/cm^{-1}): 919 (s), 1056 (vs), 1375 (m), 1440 (m), 1635 (m), 1984 (w), 2871 (vs), 2929 (vs), 3374 (s), 3305 (s). ^{1}H NMR ($CDCl_3$, 20 °C) δ: 0–2.5 (br., 40 H, peaks: 0.88, 1.26, 1.75), 3.67 (br. s, 2H), 5.2–6.5 (br., 2 H, peaks: 5.04, 5.60). Found (%): C, 68.3–88.4; H, 8.0; Br, < 0.1; Mg, < 0.1. Calc. for $(CH)_n$ (%): C, 92.31; H, 7.69.

The syntheses catalyzed by $FeCl_2$ or $CuCl_2$ were carried out in a similar way. The product yield in these cases was 72–83%.

Method B. The reaction was performed in the same way as in method A but without adding $CoBr_2$. Product yield: 70%.

© 2016 Mendeleev Communications. Published by ELSEVIER B.V. on behalf of the N. D. Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences.

insoluble fraction (so-called high-molecular-weight form[3–6]). This fact indicates that the true molecular weights of the resulting polymers can far exceed the above values.

Synthesis in a mechanical activator can be successfully used to obtain other representatives of the polycarbyne family. For example, poly(phenylcarbyne) $(\mathrm{PhC})_n$ **2**,[‡] which is also used in the synthesis of diamond coatings and phases,[3] can be obtained in high yield by reacting magnesium with trichlorotoluene $\mathrm{PhCCl_3}$ (Scheme 2).

$$2\,\mathrm{PhCCl_3} + 3\,\mathrm{Mg} \xrightarrow[-\,3\,\mathrm{MgCl_2}]{\mathrm{CoCl_2,\ THF,\ mechanical\ activation}} (\mathrm{PhC})_n$$

2

Scheme 2

The spectral characteristics of the polycarbynes synthesized are similar to those known from the literature.[3–6] The ^{1}H NMR spectrum of polymer **1** displays a broad band at δ 0–3.0 ppm, which accounts for about 90% of the total intensity of the spectrum. This band is due to the resonance of the aliphatic network, showing alkyl group peaks at 0.89, 1.27, 1.69, and 2.18 ppm. In addition, the spectrum of **1** contains weak broad bands with maxima at 3.67, 5.04, and 5.60 ppm, which are likely due to impurities. Note that a similar spectrum is observed for the polymer synthesized without employing $\mathrm{CoBr_2}$,[1] but the signals from impurities at 3.67, 5.04, and 5.60 ppm in this spectrum are almost one order of magnitude greater than the same signals in the spectrum of **1**. The ^{1}H NMR spectrum of poly(phenylcarbyne) **2** in the aromatic proton region has a strong broad resonance band at 7.20 ppm due to phenyl moieties. In the aliphatic region of the spectrum of **2**, there are weak broad bands at 1.16, 1.81, and 2.11 ppm, which are assignable to hydrogen atoms bonded to the aliphatic carbon framework. The presence of aliphatic hydrogen in **2** is usually explained by its abstraction from solvent molecules.[3–6] The observed line broadening in the ^{1}H NMR spectra of polymers **1** and **2** is caused by their paramagnetism, a common property of polycarbynes.[3–6] At 20 °C, the EPR spectrum of **1** is a singlet at $g = 2.004$ and that of **2** is a singlet at $g = 2.005$.

The IR spectrum of **1** shows an absorption band at 1058 cm^{-1}, which is due to vibrations of the aliphatic framework, and bands at 2925 and 2870 cm^{-1}, which arise from C–H stretching vibrations. The bands at 1670, 3014, and 3054 cm^{-1} are likely due to the presence of unsaturated carbon fragments. The IR spectrum of **2** exhibits strong absorption bands corresponding to vibrations of aromatic moieties at 3052 cm^{-1} (C–H bonds) and 1605 cm^{-1} (C–C bonds), as well as strong bands at 750 and 705 cm^{-1}. The absorption bands at 2930 and 2885 cm^{-1} are assignable to vibrations of impurity aliphatic C–C bonds; the bands at 1031 and 910 cm^{-1}, to vibrations of the aliphatic carbon framework.

In conclusion, the data obtained demonstrate that the use of catalyst significantly improves the characteristics of the resulting polycarbyne. Apparently, this approach can be applicable to both trihalides and polyhalides employed in polycarbyne synthesis[3,5,6] and metals other than magnesium can also be usable as the reductant.

This study was supported by the Russian Foundation for Basic Research (project no. 15-03-0697615).

References

1 A. I. Sizov, T. M. Zvukova and B. M. Bulychev, *Russ. Chem. Bull., Int. Ed.*, 2012, **61**, 668 (*Izv. Akad. Nauk, Ser. Khim.*, 2012, 665).
2 O. A. Reutov, I. P. Beletskaya, G. A. Artamkina and A. N. Kashin, *Reaktsii metalloorganicheskikh soedinenii kak redoks-protsessy (Reactions of Organometallic Compounds as Redox Processes)*, Nauka, Moscow, 1981 (in Russian).
3 G. T. Visscher and P. A. Bianconi, *J. Am. Chem. Soc.*, 1994, **116**, 1805.
4 P. A. Bianconi, S. J. Joray, B. L. Aldrich, J. Sumranjit, D. J. Duffy, D. P. Long, J. L. Lazorcik, L. Raboin, J. K. Kearns, S. L. Smulligan and J. M. Babyak, *J. Am. Chem. Soc.*, 2004, **126**, 3191.
5 Y. Nur, M. W. Pitcher, S. Seyyidoglu and L. Toppare, *J. Macromol. Sci., Part A: Pure Appl. Chem.*, 2008, **45**, 358.
6 Y. Nur, H. M. Cengiz, M. W. Pitcher and L. K. Toppare, *J. Mater. Sci.*, 2009, **44**, 2774.

Received: 1st July 2015; Com. 15/4666

[‡] *Synthesis of poly(phenylcarbyne)* **2**. The synthesis was carried out in the same manner as the synthesis of polymer **1** by method A. Reagents $\mathrm{PhCCl_3}$ (2.4 g, 12.3 mmol), magnesium (0.8 g, 33.3 mmol), $\mathrm{CoCl_2}$ (50 mg), and THF (40 ml) were placed in the jar of the activator. The reaction was conducted at 15 °C for 6 min. The product was washed with water and then precipitated from THF (8 ml) with methanol (50 ml). A brown powder was thus obtained (0.87 g, 80% yield). IR (KBr, ν/cm^{-1}): 852 (s), 1027 (s), 1097 (s), 1261 (vs), 1377 (s), 1641 (w), 2855 (vs), 2932 (s), 2969 (s). ^{1}H NMR ($\mathrm{CDCl_3}$, 20 °C) δ: 1.16 (br. s, 2H), 1.81 (br. s, 2H), 2.11 (br. s, 2H), 7.20 (br., 90H). Found (%): C, 89.2; H, 6.0; Cl, < 0.1; Mg, < 0.1. Calc. for $(\mathrm{C_7H_5})_n$ (%): C, 94.38; H, 5.62.