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Microstructure and morphology of polyphenylacetylene prepared in compressed carbon dioxide†

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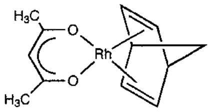
Polyphenylacetylene was prepared by transition metal catalysis in compressed (liquid and supercritical) CO_2. Surface morphology, IR and NMR spectroscopic properties of the resulting materials are discussed in terms of the microstructure of polymers. Copyright © 2001 John Wiley & Sons, Ltd.

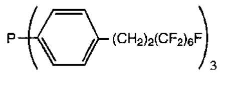
Keywords: polyphenylacetylene; carbon dioxide; rhodium catalyst

INTRODUCTION

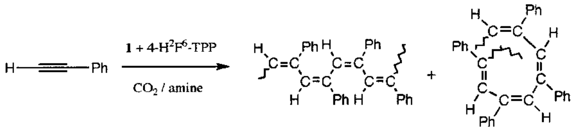
Compressed (liquid or supercritical state) CO_2 has been recognized as an innovative and ecologically benign reaction medium for chemical synthesis.[1] Polymerization in such a reaction medium has received particular attention owing to the potential for controlling the morphology and microstructure of the resulting polymers.[2] Indeed, evaluation for commercial-scale manufacture of fluoropolymers in compressed CO_2 has been started.[3] We have recently demonstrated that polymerization of phenylacetylene (PA) can be achieved in compressed CO_2 by using a rhodium catalyst [(acac)Rh(nbd)] (acac = acetyl acetonate, nbd = 2,5-norbornadiene) (**1**).[4] In the present work, we prepared polyphenylacetylene (PPA) by using **1** and the 'CO_2-philic' ligand $\{4\text{-}F(CF_2)_6(CH_2)_2C_6H_4\}_3P$ (4-H^2F^6-TPP) and then examined the surface morphology and spectroscopic properties of the resulting polymers.



[(acac)Rh(nbd)] (**1**)



4-H^2F^6-TPP



PA cis-transoidal PPA cis-cisoidal PPA

RESULTS AND DISCUSSION

When CO_2 (10–24 g) was introduced into a window-equipped high-pressure reactor (27 ml) containing a mixture of **1** (7 mg, 23 μmol), 4-H^2F^6-TPP (30 mg, 23 μmol) and quinuclidine (26 mg, 230 μmol) at room temperature, a bright orange homogeneous solution was formed (Fig. 1a). Upon addition of PA (0.46 g, 4.5 mmol), polymerization occurred both at room temperature and at 40 °C, as indicated by a bright orange precipitate (Fig. 1b). The resulting PPA consisted of two species: one is yellow and soluble in THF,

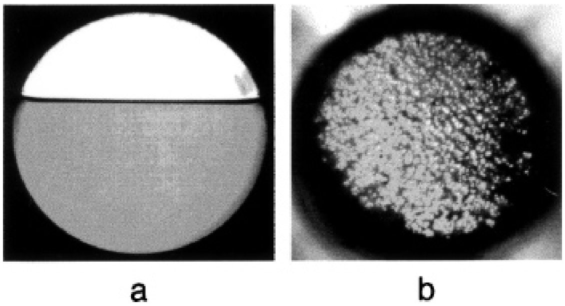


Figure 1 Photographs showing the interior of the window-equipped high-pressure reactor: (a) before PA introduction (22 °C, 58 bar); (b) after heating and PA introduction (43 °C, 110 bar).

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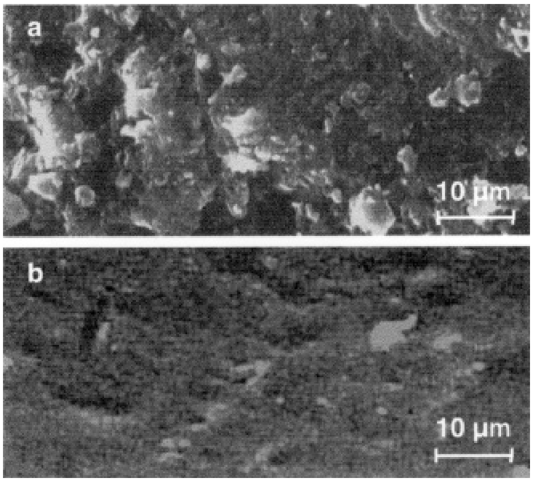

Figure 2 SEM images of (a) THF-soluble and (b) THF-insoluble PPA prepared in compressed CO_2.

whereas the other is deep red and not soluble in any organic solvents. The total yield was 76% and the ratio of soluble to insoluble species was 42:58 when the reaction was carried out in liquid CO_2 (26 °C, 94 bar). Changes of pressure and temperature affected the product ratio, leading for example to a ratio of 24:76 at 41 °C and 187 bar. The THF-soluble species had a weight-averaged molecular weight of approximately 4×10^4 and a broad molecular weight distribution (M_w/M_n) of approximately 8.8, relative to polystyrene as a standard. Figure 2 shows the surface morphology of the two different fractions of PPA as revealed by scanning electron microscopy(SEM). The soluble species is fragile and the surface is rough (Fig. 2a). On the other hand, the insoluble species showed a more compact and smooth structure (Fig. 2b), which may be partly responsible for the poor solubility.

The stereoregularity of PPA is reflected in the IR spectra. Generally, PPA has two absorption bands at 740 and 760 cm^{-1} and the content of cis and trans units has been evaluated by the ratio of the intensities of the two bands.[5–7] The trans-rich PPA shows no absorption at 740 cm^{-1}, but shows absorption at 760 cm^{-1}. On the other hand, cis-rich PPA shows both absorption bands, and a higher stereoregularity (cis content) results in higher intensity of the band at 740 cm^{-1}. Figure 3a shows the IR spectrum of THF-insoluble PPA prepared in liquid CO_2. The presence of two bands at 740 and 760 cm^{-1} indicates that the insoluble species is cis-rich PPA. Taking into account the solubility properties, this material is identified to consist mainly of cis-cisoidal PPA. Figure 3b shows the IR spectrum of THF-soluble PPA. The doublet at 740 and 760 cm^{-1} also appeared and the former is stronger than the latter, suggesting that this species is also cis-rich PPA, with higher stereoregularity than the insoluble polymer.

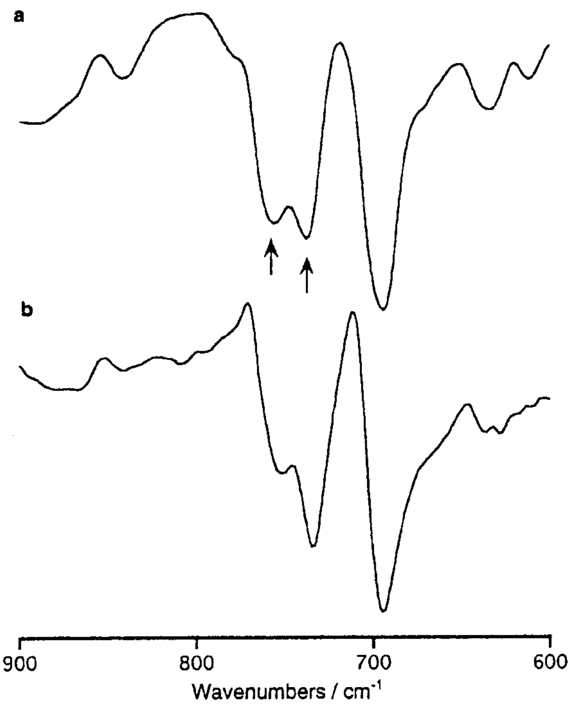

Figure 3 IR (KBr) spectra of (a) THF-insoluble and (b) THF-soluble PPA prepared in compressed CO_2.

NMR measurements provided additional information on the stereochemistry of the soluble PPA.[8–10] Figure 4 shows the ^1H-NMR spectrum (in $CDCl_3$) of the THF-soluble PPA prepared in liquid CO_2. The soluble polymer showed signals at δ 5.82 (s, 1H, vinyl proton), 6.60–6.62 (m, 2H, ortho aromatic protons), and 6.88–6.93 (m, 3H, meta and para aromatic protons). It also showed signals at δ 126.70, 127.58, 127.80, 131.79, 139.36 and 142.90 in the $^{13}C\{^1H\}$ NMR spectrum. These values indicate that the THF-soluble material consists mainly of cis-transoidal PPA. The ratio of the intensity of the vinyl resonance to the total area of proton resonances is frequently used as a quantitative parameter for the stereoregularity, i.e. cis-content.[6,9]

$$\text{cis}\ (\%) = [A_{5.82}/(A_{\text{total}})/6] \times 100$$

where $A_{5.82}$ is the area of the vinyl proton and A_{total}

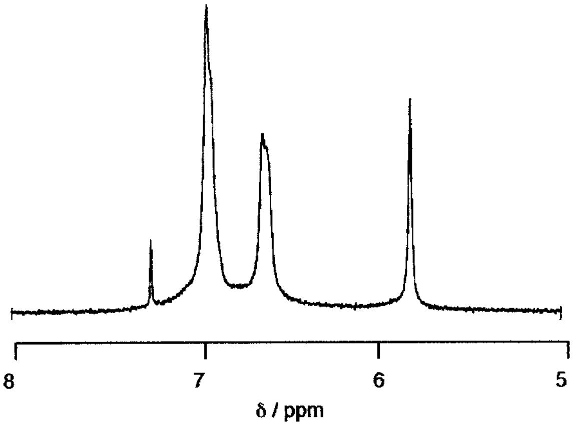

Figure 4 ^{1}H-NMR spectrum of THF-soluble PPA prepared in compressed CO_2.

is the total area of the spectrum. According to this analysis, the THF-soluble PPA prepared in liquid CO_2 showed a cis-content of 90%. This value is almost the same as those obtained in conventional organic solvents using **1** in the absence 4-H^2F^6-TPP at room temperature and normal pressure, e.g. 88% for THF and 85% for hexane. Hence, the cis-transoidal PPA prepared in compressed CO_2 has at least the same stereoregularity as that prepared in conventional organic solvents.

CONCLUSION

We have demonstrated that PA polymerization can be carried out in compressed CO_2 as an environmentally friendly reaction medium using rhodium catalyst **1** in the presence of the ligand 4-H^2F^6-TPP. The resulting polymers consisted of THF-soluble and THF-insoluble material. The former was identified as mainly cis-transoidal PPA and the latter as cis-cisoidal PPA. The stereoregularity of the THF-soluble polymer is comparable to that obtained in conventional organic solvents. For PA polymerization in conventional solvents, novel rhodium catalysts were recently reported to cause living polymerizations leading to very narrow molecular-weight distribution and high stereoregularity.[10] It seems highly rewarding for future work to combine such catalysts with 4-H^2F^6-TPP to achieve living polymerization of PA also in compressed CO_2.

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