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Addition Polymers of Strained Cyclic Olefins – Transition Metal Catalysed Polymerisations of the Cyclobutene Derivative Bicyclo[3.2.0]hept-6-ene

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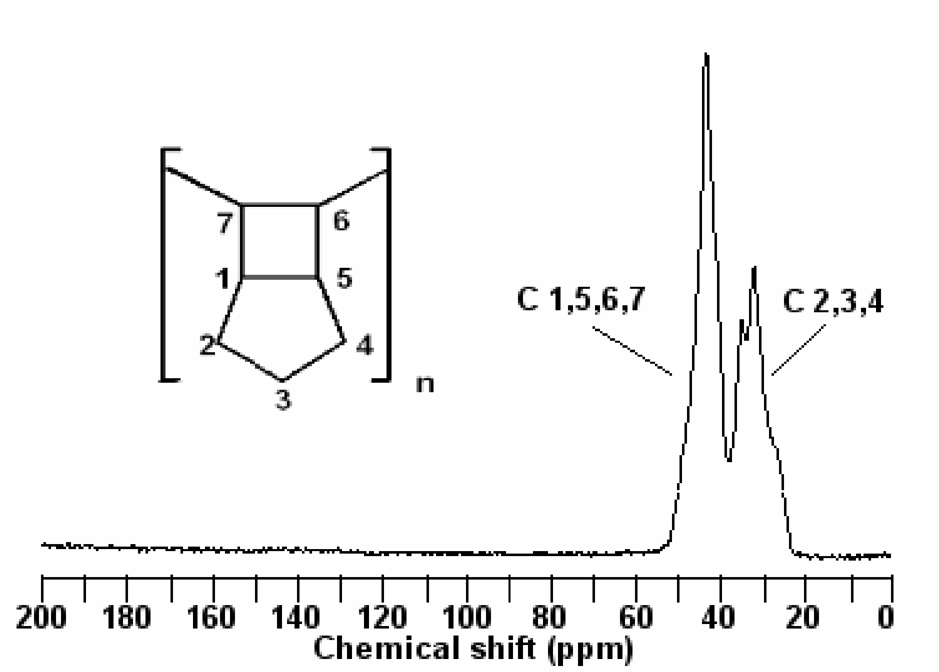

Figure 1. Solid state ^{13}C NMR spectrum of polymer **4** produced using complex **7**, [Mon]/[Pd] = 50/1 (entry no. 4, Table 1).

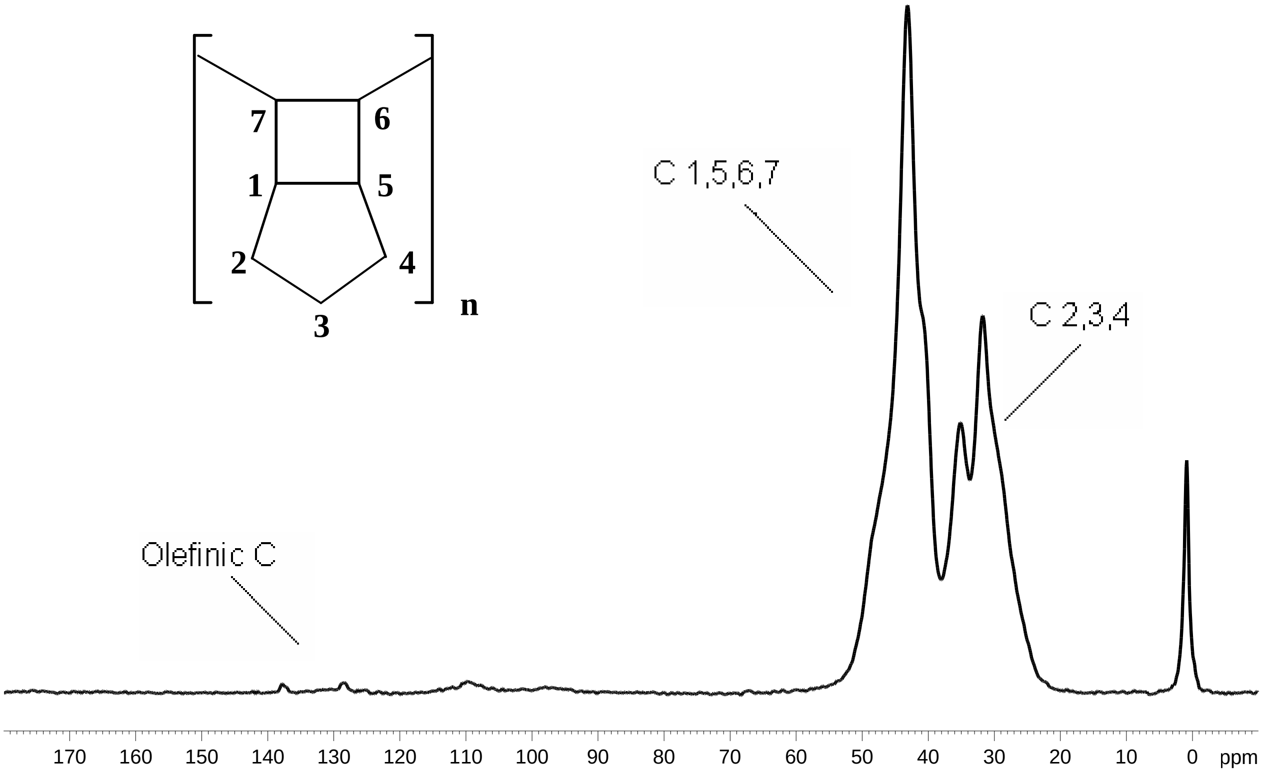

Figure 2. Solid state ^{13}C NMR spectrum of polymer **4** produced using complex **9**, [Mon]/[Al]/[Zr] = 250/200/1 (entry no. 9, Table 1) (spinning side bands between δ95 and 115 ppm).

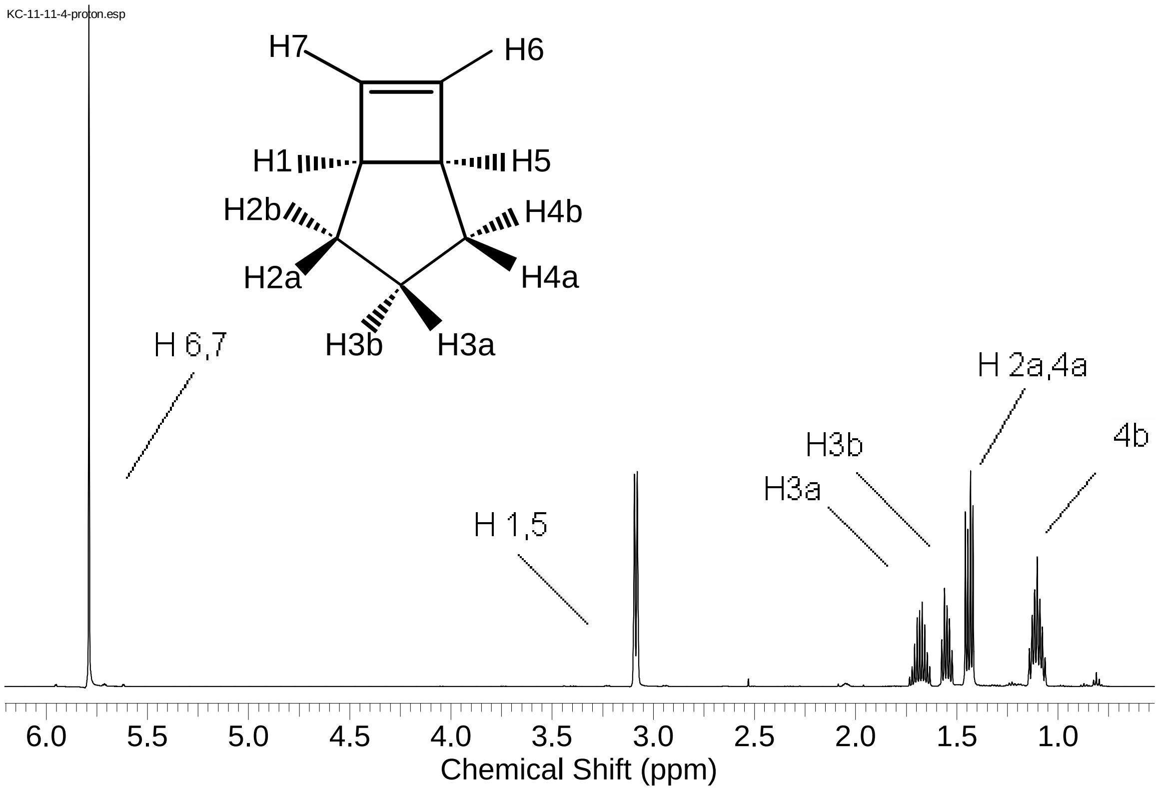

Figure 3. ^{1}H NMR spectrum of bicyclo[3.2.0]hept-6-ene, **3**, used in polymerisation reactions, solvent: $CDCl_3$.

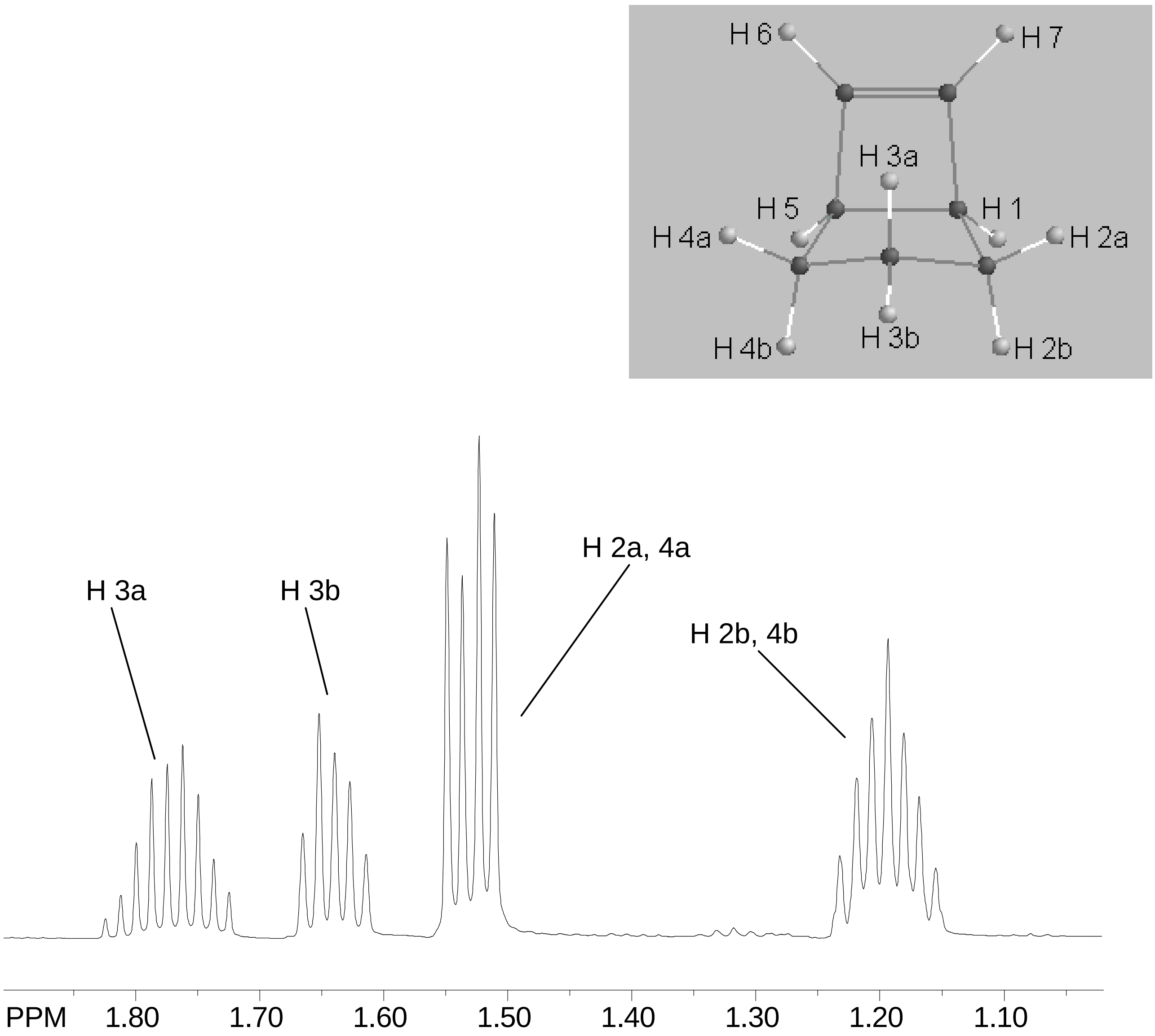

Figure 4. ^{1}H NMR spectrum of bicyclo[3.2.0]hept-6-ene, **3**, close up of CH_2 region, solvent: $CDCl_3$.

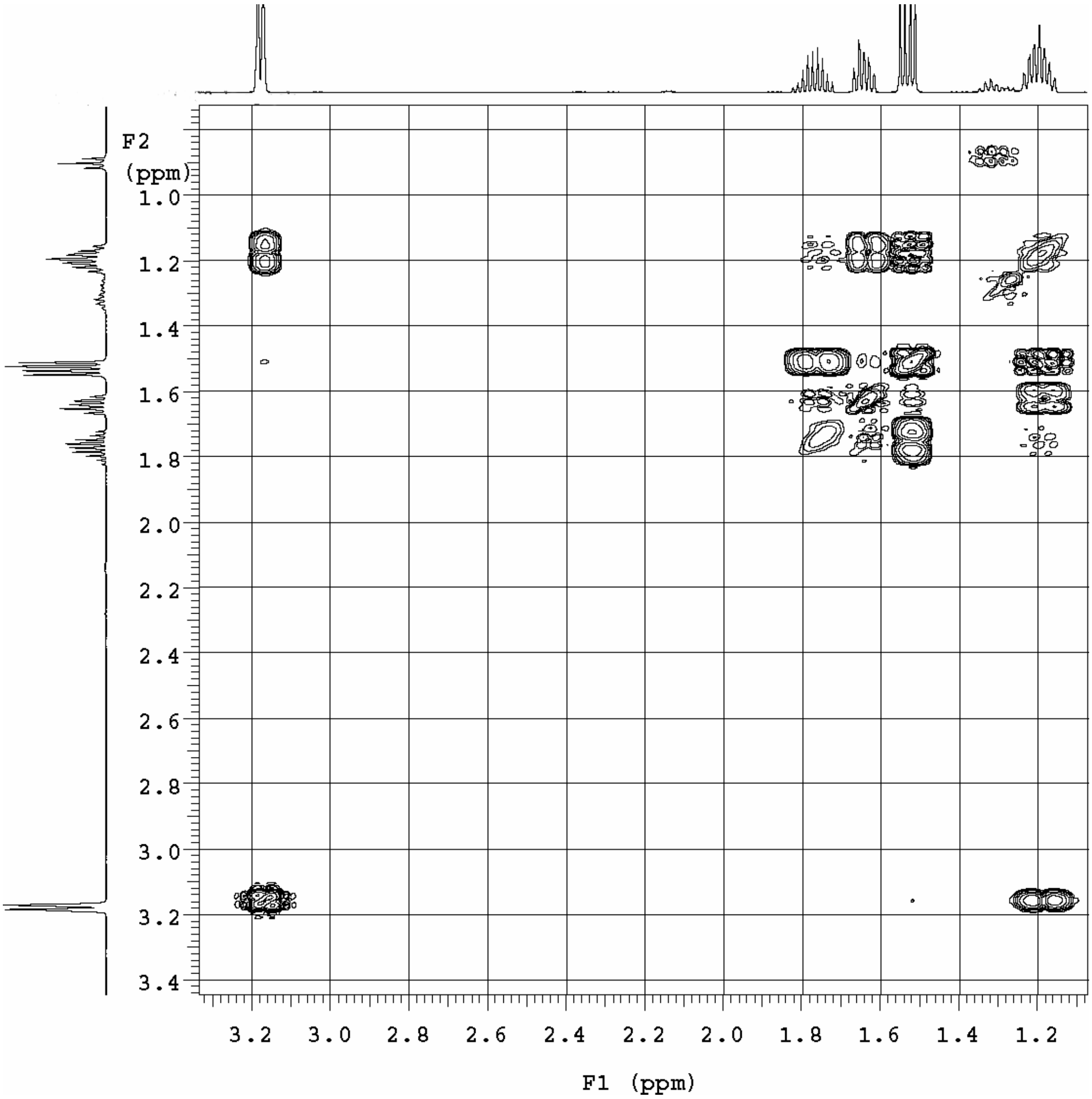

Figure 5. ^1H-^1H COSY NMR spectrum of bicyclo[3.2.0]hept-6-ene, **3**, solvent = $CDCl_3$.

It was possible to determine the predominant conformation of the monomer from its ^1H NMR spectrum. The coupling pattern of the bridgehead protons $H^{1,5}$ is discussed in the main body of the paper. Furthermore, the two protons H^{2a} and H^{4a} produce a characteristically simple coupling pattern of a doublet of doublet (dd) at $\delta = 1.53$ ppm (Figure 4). They show a geminal coupling J_1 of 12.7 Hz with H^{2b} and H^{4b} and a vicinal coupling J_2 of 6.1 Hz with H^{3a}. The ^1H-^1H COSY spectrum (Figure 5) does not show any correlation between $H^{2a,4a}$ and $H^{1,5}$ and only a very weak correlation between $H^{2a,4a}$ and H^{3b}. This shows that both the dihedral angle that is formed between H^{2a} and H^1 (H2b-C2-C1-H1) and the dihedral angle that is formed between

$H^{2a \text{ and }}H^{3b}$(H2a-C2-C3-H3b) are approximately 90°, according to the Karplus equation.[1] This indicates that the boat conformation is prevailing. The predominance of the boat conformer is further confirmed by the coupling patterns of the other protons: dddd for H^{2b} and H^{4b} with $J_1 = J_2 = 12.7$ Hz and $J_3 = J_4 = 6.1$ Hz; dt for H^{3b} with $J_1 = 12.7$ Hz and $J_2 = 6.1$ Hz; dtt for H^{3a} with $J_1 = J_2 = 12.7$ Hz and $J_3 = 6.1$ Hz (Figure 4). The boat and chair conformations of bicyclo[3.2.0]hept-6-ene are displayed in Figure 6 in the main body of the paper.

We conclude that at polymerisation temperatures between 20 and 70 °C, bicyclo[3.2.0]hept-6-ene exists mainly in the boat conformation. This is also confirmed by ab initio calculations reported by Qin et al. They show that the boat conformation is 4.0 $\text{kcal}\cdot\text{mol}^{-1}$ more stable than the chair conformation,[2] which corresponds to a theoretical boat to chair ratio of 860 to 1 at 293 K.

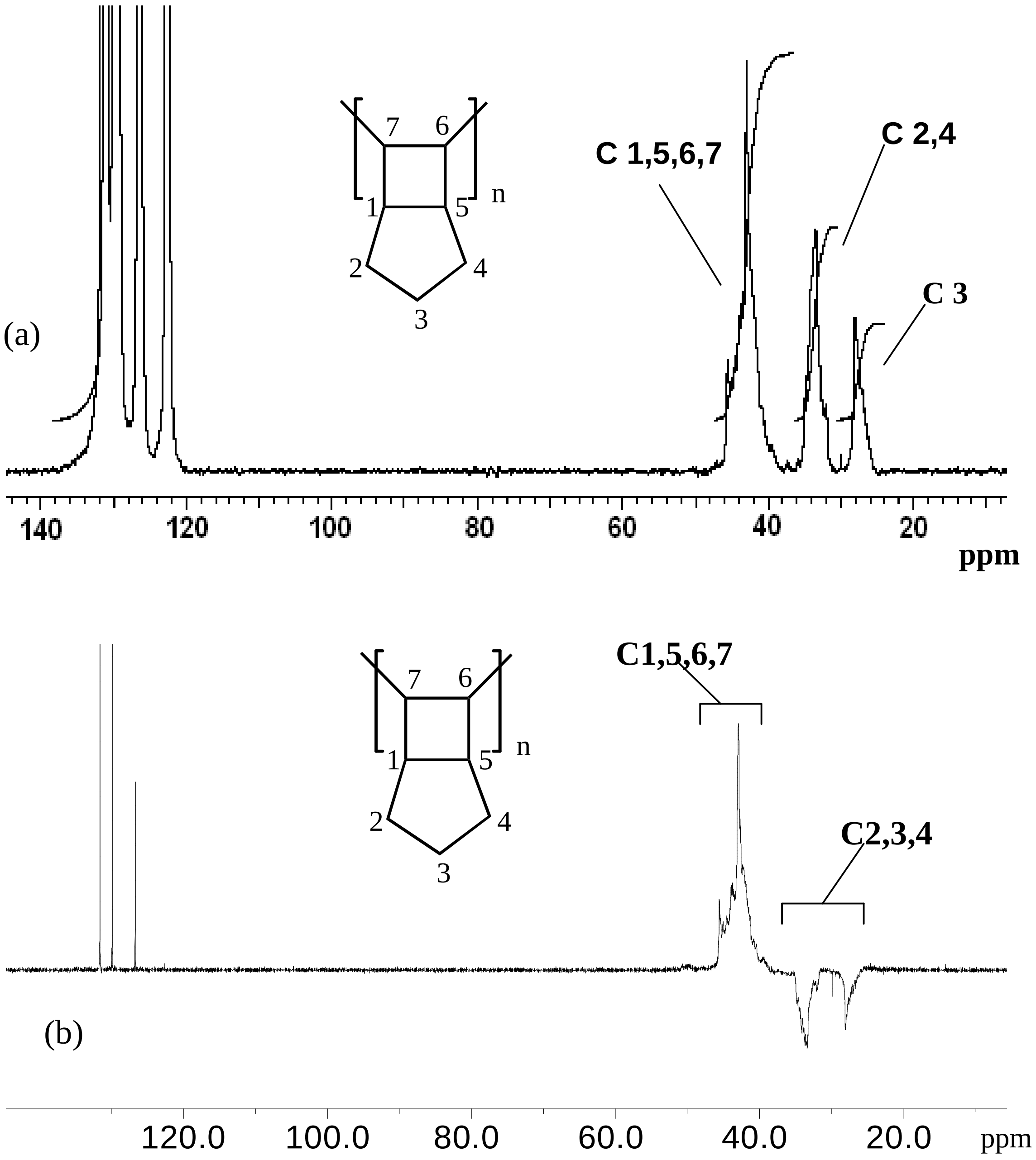

Figure 6. (a) ^{13}C NMR and (b) DEPT-135 NMR spectra of polymer **4**, produced using complex **6**, [Mon]/[Pd] = 50/1 (entry no. 1, Table 1), solvent: bromobenzene-d_5, T = 80 °C, 40 mM $Cr(acac)_3$ relaxation agent. The signals in the range of δ= 123–132 ppm are the bromobenzene-d_5 solvent signals. Assignments were made with the aid of ^{13}C NMR data reported for bicyclo[3.2.0]heptane[3] and increment values for hydrocarbon substituents.[4]

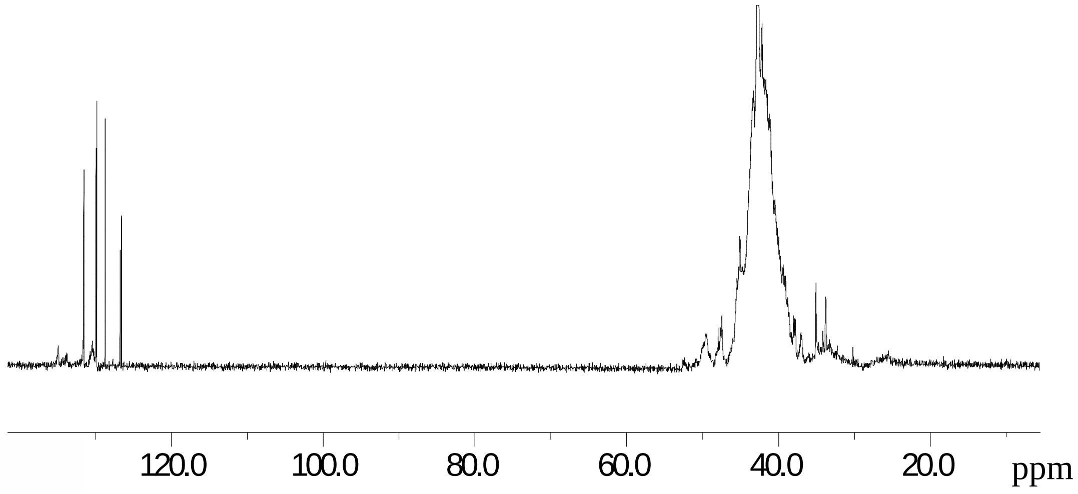

Figure 7. DEPT-90 NMR spectrum of polymer **4**, produced using complex **6**, [Mon]/[Pd] = 50/1 (entry no. 1, Table 1), solvent: bromobenzene-d_5, T = 80 °C. The signals in the range of δ= 123–132 ppm are the bromobenzene-d_5 solvent signals (traces of residual CH_2 – based signals between δ 36 and 26 ppm correspond to $C^{2,3}$).

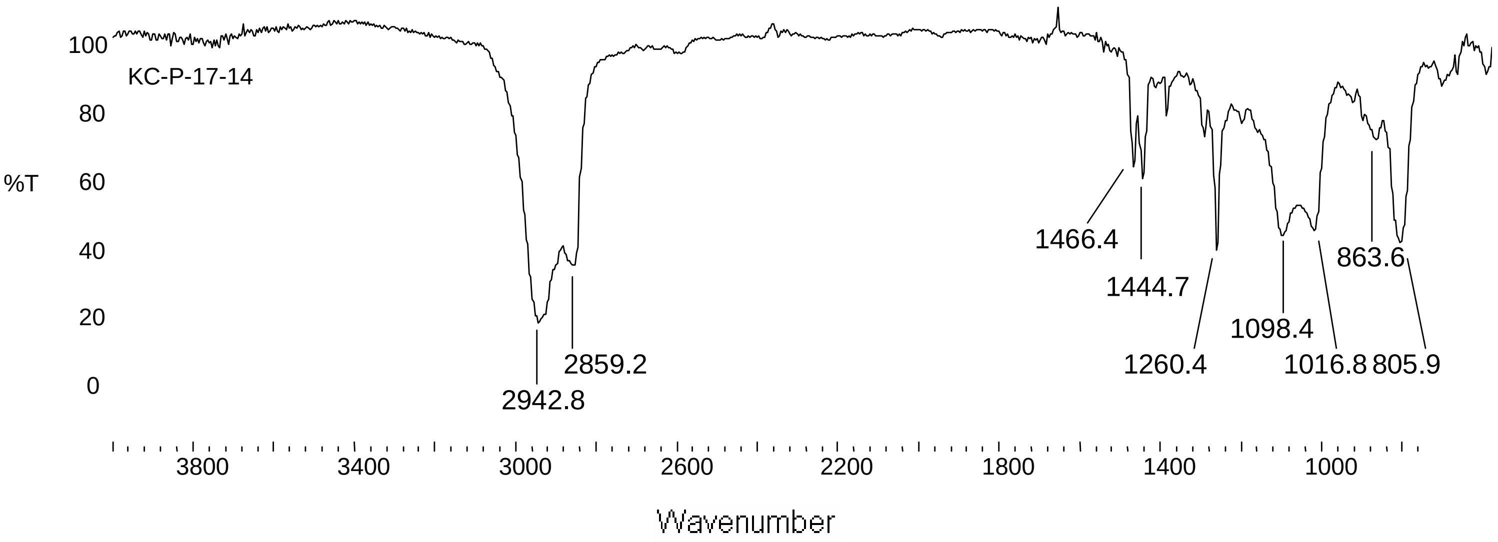

Figure 8. IR spectrum of polymer **4** produced using complex **6**, [Mon]/[Pd] = 250/1 (entry no. 3, Table 1).

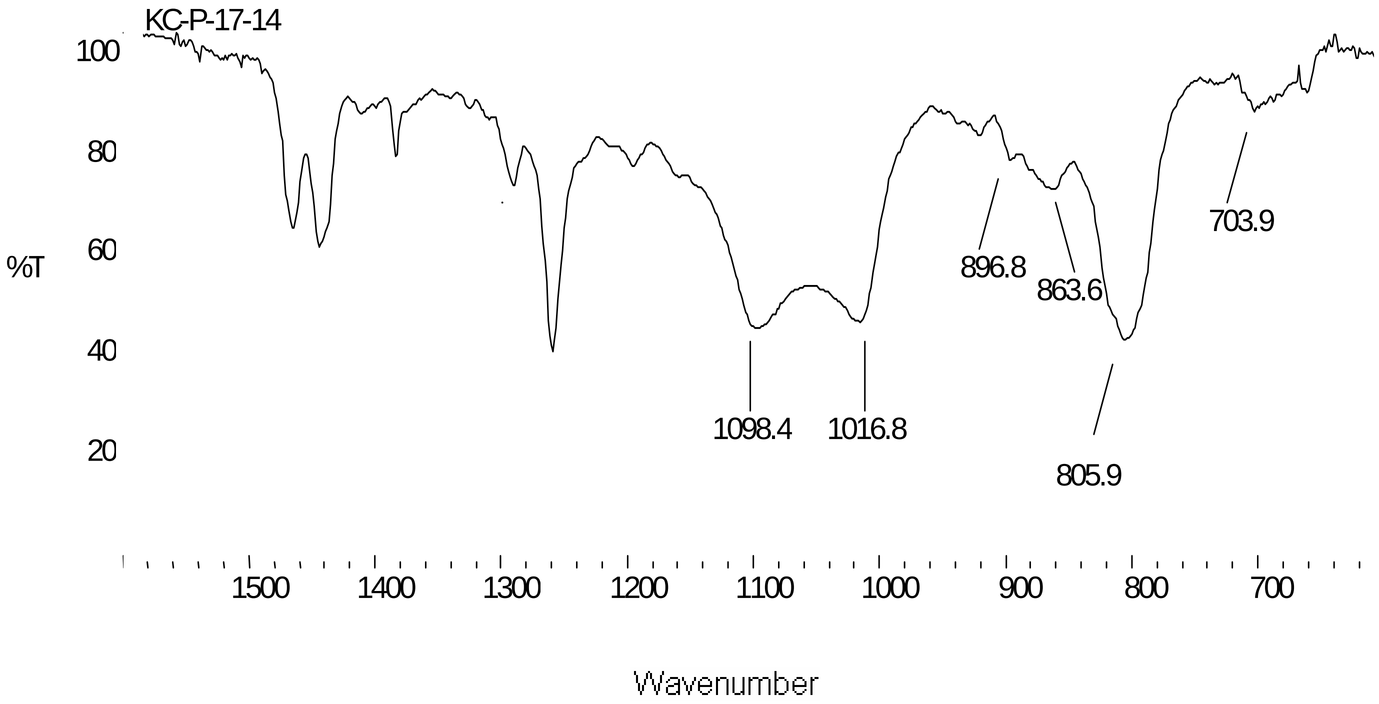

Figure 9. IR spectrum (close up of 600–1 600 cm^{-1} region) of polymer **4** produced using complex **6**, [Mon]/[Pd] = 250/1 (entry no. 3, Table 1).

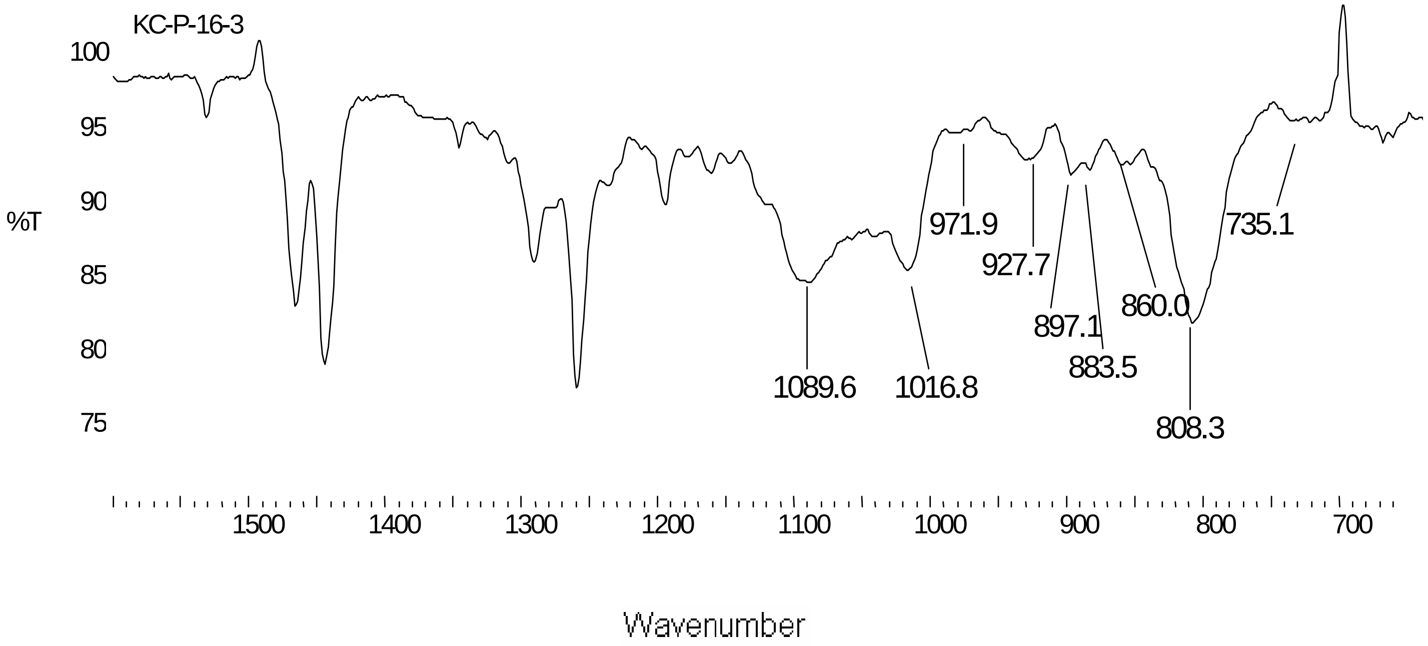

Figure 10. IR spectrum (600–1 700 cm^{-1} region) of polymer **4** produced using complex **7**, [Mon]/[Pd] = 50/1 (entry no. 4, Table 1).

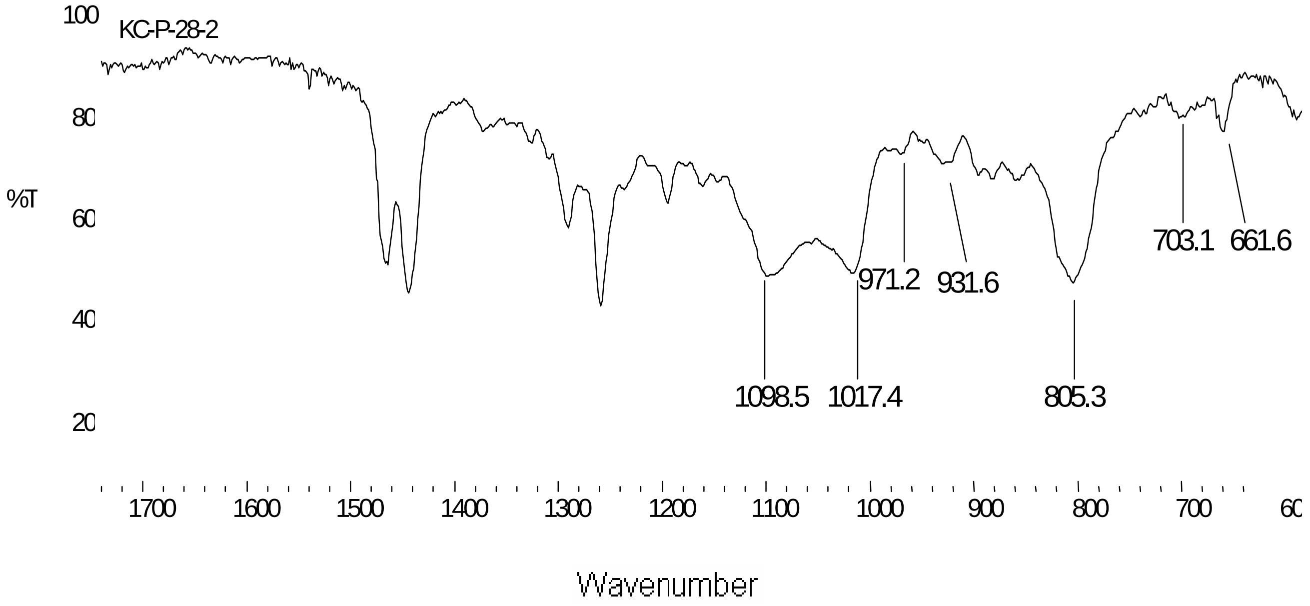

Figure 11. IR spectrum (600–1 750 cm^{-1} region) of polymer **4** produced using complex **8**, [Mon]/[Pd] = 50/1 (entry no. 7, Table 1).

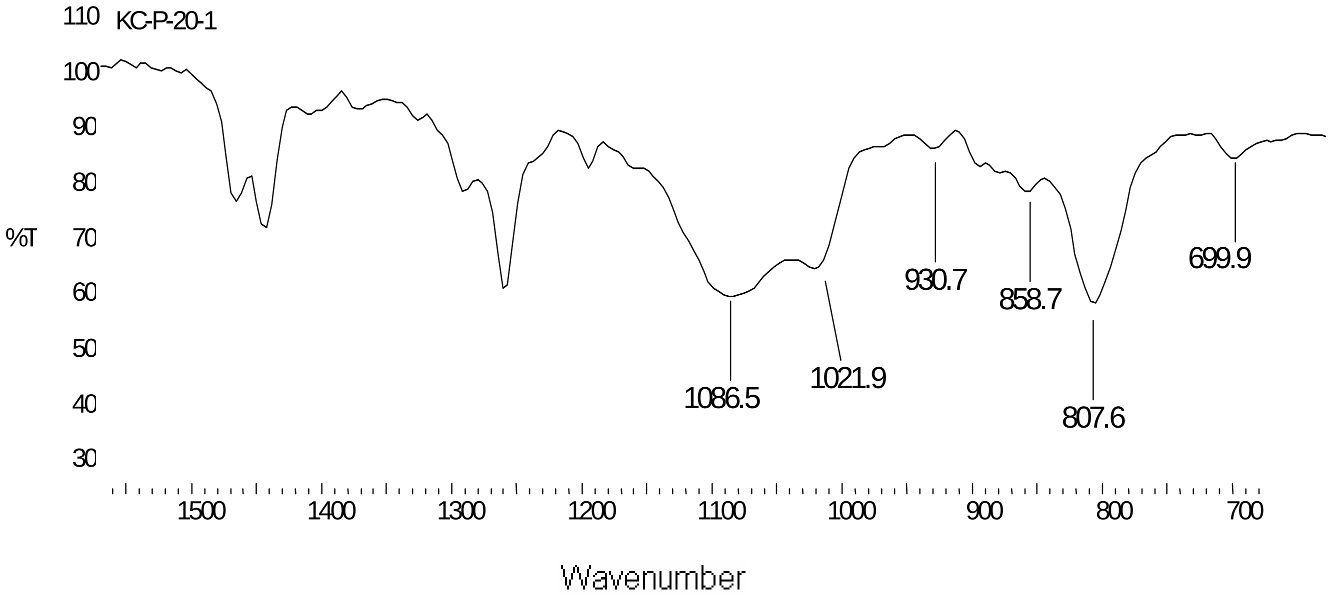

Figure 12. IR spectrum (650–1 600 cm^{-1} region) of polymer **4** produced using Cp_2ZrCl_2/MAO, [Mon]/[Al]/[Zr] =250/200/1 (entry no. 9, Table 1).

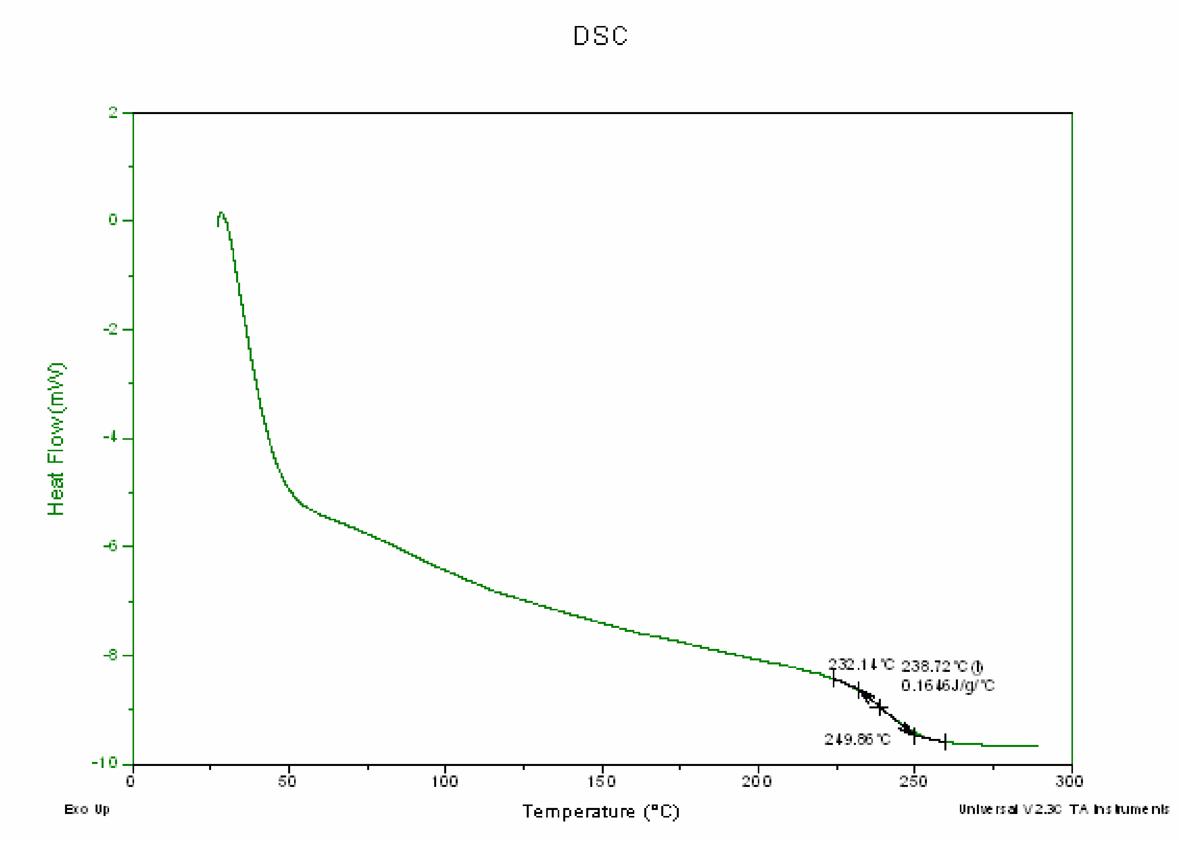

Figure 13. DSC analysis of polymer **4** (entry no. 2, Table 1), heating rate 30 K·min^{-1}, second heat run displays a T_g of 239 °C.

[1] M. Karplus, *J. Chem. Phys.* **1959**, *30*, 11.

[2] C. Qin, S. R. Davis, *Int. J. Quant. Chem.* **2004**, *96*, 432.

[3] M. W. Bouwkamp, A. C. Bowman, E. Lobkovsky, P. J. Chinik, *J. Am. Chem. Soc*. **2006**, *128*, 13340.

[4] H.-O. Kalinowski, S. Berger, S. Braun, "Carbon-13 NMR Spectroscopy", Wiley, Chichester 1988.