

Pressure-induced polymerization of phenoxyethyl acrylate

K Kaminski¹, R Wrzalik¹, M Paluch¹, J Ziolo¹ and C M Roland²

¹ Institute of Physics, Silesian University, Uniwersytecka 4, 40-007 Katowice, Poland

² Naval Research Laboratory, Chemistry Division, Code 6120, Washington, DC 20375-5342, USA

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Abstract

Polymerization of phenoxyethyl acrylate was induced without catalyst or initiators by the application of hydrostatic pressure at elevated temperature. Broadband dielectric and infrared spectroscopy were employed to follow the course of the reaction, which reached a degree of conversion of 60%. The structure of the obtained polymer was determined from density functional theory calculations.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Polymers are materials of enormous importance in various industries (food, pharmaceutical, medical, construction, electrical, etc). Often this is due to the performance advantages in comparison to more traditional materials, although the latter are often more costly as well. The demand for polymers has led to efforts to develop improved synthetic methods. Conventional polymerization relies on catalyst-promoted thermal activation, irradiation, oxidation, etc [1–3], although alternative methods are used [4, 5]. One promising approach is polymerization induced only by the application of large hydrostatic pressure. This method has obvious advantages: (i) the product tends to be of high purity; (ii) waste and toxicity aspects of catalysts are avoided; (iii) the reaction is performed in bulk without solvents; and (iv) potentially materials can be made that are unattainable at ambient pressure. There have been a few publications describing pressure-induced polymerization in unsaturated, hydrocarbons such as ethylene [6, 7], propylene [8], benzene [9, 10], isoprene [11, 12], styrene [13], and butadiene [2, 14]. In the case of ethylene, isoprene, and butadiene, laser irradiation of the system under high pressure can lead to new reaction pathways, producing unique polymer products. Nevertheless, further studies are required to clarify the reaction mechanisms, so that new syntheses can be developed and exploited.

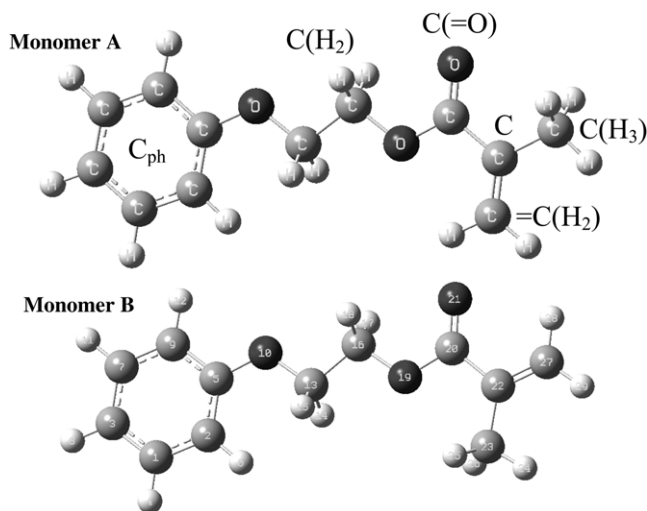
In this paper we describe polymerization of the phenoxyethyl acrylate. Acrylate polymers, found in many different applications, are conventionally synthesized at high temperatures with catalysts or, in the case of free radical

polymerization, with organic peroxides [15–18]. The only example of pressure-induced polymerization was earlier work of our group on tetraethylene glycol dimethacrylate (TEGDMA) polymerization [19]. In that case, the reaction was accompanied by significant crosslinking, leading to a network structure in the obtained polymer. With phenoxyethyl acrylate only linear polymerization is possible, since unlike TEGDMA phenoxyethyl acrylate has only one double bonds.

The main techniques used in our investigation were dielectric and infrared (IR) spectroscopy. The first is commonly used to measure the dynamics of polymers. It can be also used to monitor polymerization, since during the reaction there is a decrease of the dc conductivity due to reduced diffusivity of ions. Simultaneously there is an increase in the local segmental (α -) relaxation time of the main species due to its increasing size and more constrained nature. This means that the glass transition temperature, T_g , of the reacting system also increases during polymerization. IR spectroscopy allows the identification of the reaction products, as well as the moieties involved in the polymerization, which is informative concerning the reaction mechanism.

2. Experimental details

The phenoxyethyl acrylate (98% purity) was received from Sartomer Company. Polymerization. Briefly, the procedure involved filling the dielectric cell with the monomer liquid, and then placing it into a Teflon bellows mounted in the high pressure chamber. Hydrostatic pressure was generated



Scheme 1. Structure of monomer A and monomer B with atom numbering and symbols used in table 1.

by displacing a piston via a hydraulic press. Pressure was calculated from the force exerted on the piston (accuracy ~ 10 MPa).

IR measurements used a Bio-Rad FTS-6000 spectrometer equipped with a KBr beam splitter, a standard source, and a DTGS Peltier-cooled detector. The MIRacle diamond accessory with a KRS5 prism was used to collect spectra in the range $380\text{--}4000\text{ cm}^{-1}$ with 2 cm^{-1} resolution. Generally 32 scans were accumulated to achieve sufficient quality spectra.

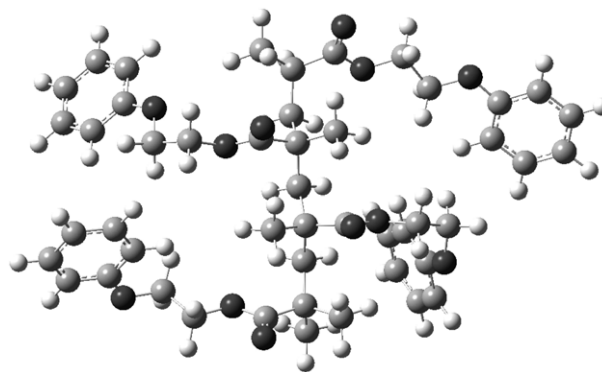
3. Calculations

Ab initio calculations were performed with the PQS program. Geometry optimization and IR spectra were calculated using density functional theory (DFT); the B3LYP functional and standard Gaussian polarized and split-valence basis set (6-31G*) were applied. The harmonic vibrational frequencies and IR intensities were recalculated using Pulay's scaled quantum mechanical force field (SQM) methodology [20]. This procedure gives good reproduction of the fundamental frequencies and allows band assignments.

The calculations were done for two conformers of the phenoxyethyl acrylate molecule (monomer A and B) and the polymer derived from four monomers, as seen in schemes 1 and 2, respectively. To compare the theoretical and experimental results more easily, the theoretical spectra were constructed as a sum of Lorentz bands with 5 cm^{-1} full width at half-maximum.

4. Results and discussion

An initial pressure of 1 GPa was applied at $T = 373\text{ K}$. During the reaction a significant drop in pressure was observed, since polymerization reduces the volume of the material. The recovered product had a rubber-solid form, clear evidence that the liquid monomer had polymerized.



Scheme 2. Structure of the polymer composed of four phenoxyethyl acrylate monomers.

In figure 1 are shown the dielectric loss spectra of the monomer (left upper panel) and polymer after 15 h reaction (right upper panel). The spectra are above T_g , defined as the temperature at which $\tau_\alpha = 100\text{ s}$. For both materials a primary α -relaxation process and the dc conductivity are evident in the spectra; these move toward lower frequencies with decreasing temperature. In addition a secondary relaxation process becomes apparent at lower temperatures for both monomer and product.

In the lower panel of figure 1 representative loss spectra of the monomer and polymer measured respectively at $T = 215$ and 211 K and at $T = 297$ and 285 K are shown (note the dc conductivity was subtracted for clarity). At these temperatures the polymer and monomer have the same τ_α . The shifting of τ_α to higher temperature reflects the larger molecular weight of the product. The width of the α -relaxation peak of the polymer is also broader than that of the monomer, in addition to some broadening with decreasing temperature. The loss spectra for the polymer also has a significantly greater dc contribution. This may originate from unreacted monomers. Note that in the range of temperatures where the α -relaxation of the polymer is observed, there is a large dc conductivity in the loss spectrum of the phenoxyethyl acrylate.

In figure 2 the temperature dependence of the α -relaxation times of polymer and monomer are compared. $\tau_\alpha(T)$ data were fitted by the VFT equation:

$$\tau_\alpha = \tau_{\text{VFT}} \exp\left[D/(T - T_0)\right], \quad (1)$$

from which the glass transition temperatures were determined, equal to 194 and 245 K for the monomer and polymer respectively. Of course, T_g is larger for the polymer than the corresponding monomer [21, 22]. The large difference (50 K) in the present case suggests the product has a substantial molecular weight.

The fragilities of the monomer and polymer were determined as:

$$m = d \log_{10} \tau_\alpha / d(T_g/T)|_{(T_g/T)=1} \quad (2)$$

with the surprising result that $m = 46$ for the polymer, a small value and much less than for the monomer, $m = 79$. Below the high polymer limit fragility increases with

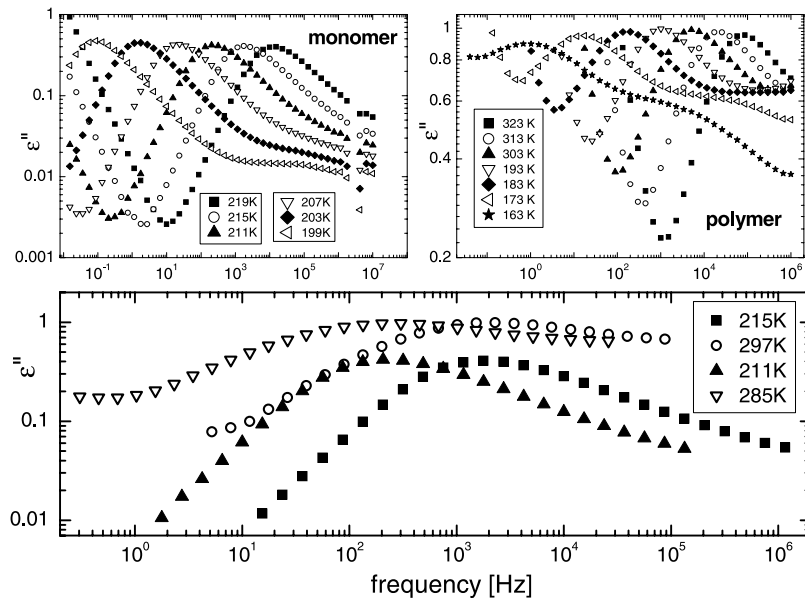


Figure 1. Left and right upper panels: dielectric loss curves for monomer and polymer at 0.1 MPa. Lower panel: dielectric loss spectra of the monomer measured at $T = 215$ and 211 K (filled symbols) and the polymer at $T = 297$ and 285 K (open symbols). The dc conductivity has been subtracted.

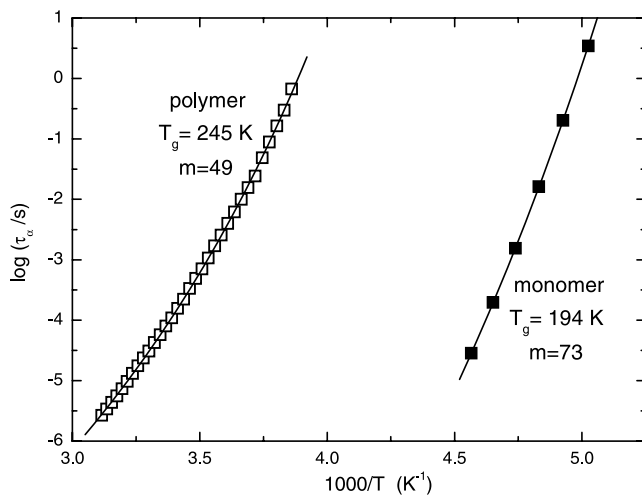


Figure 2. Arrhenius plot of the dielectric α -relaxation times for the phenoxyethyl acrylate (filled squares) and polymer (open squares). The solid lines are VFT fits.

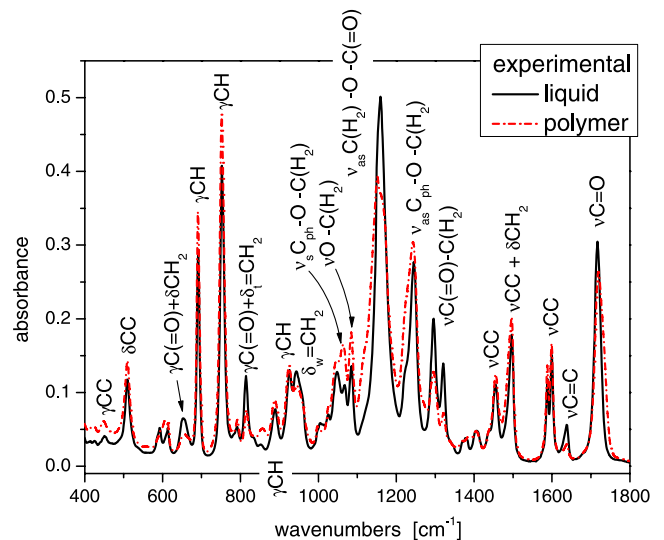


Figure 3. IR spectra of the phenoxyethyl acrylate (solid line) and polymer (dotted line) showing the vibrational assignments.

molecular weight [22]. The only exception is polyisobutylene, for which was shown recently that over a range of molecular weight, m decreases with molecular weight [23]. We speculate that the peculiar result herein is due to steric hindrance of the polymer. As can be seen in scheme 2, the geometry of the polymer, composed by phenoxyethyl acrylate monomer units, is rather complex.

To summarize this part of the work, dielectric measurements show that phenoxyethyl acrylate undergoes polymerization to a substantial molecular weight at 1 GPa and 373 K. Next we focus on IR measurements to describe the structure of the polymer and estimate the degree of conversion. FTIR spectra of the phenoxyethyl acrylate monomer and polymer are shown

in figure 3. The spectra are rather similar, although differences are present. The most important changes are for the bands at 1637, 1321, 1286, 1151, 1064, 945, 814, and 656 cm^{-1} . To assign the fundamental vibrations of these absorptions, DFT vibrational spectra calculations were carried out.

As depicted in figure 4, the calculated IR spectra for the phenoxyethyl acrylate monomer (upper curves) reproduces well the position of the bands. However, in the frequency range 1370–1230 cm^{-1} two peaks are observed for the experimental spectra, whereas there is only one in the calculated spectra. To investigate this we made additional calculations for the monomer with antiparallel alignment of

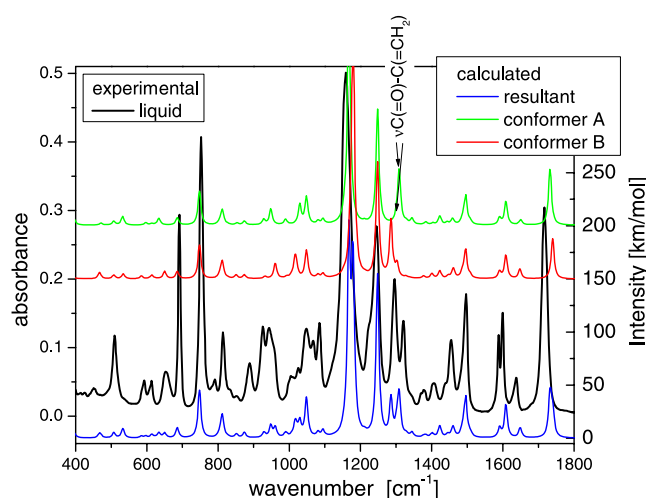


Figure 4. Calculated IR spectrum for monomer A (green solid line) and B (red solid line), sum of the two calculated spectra (blue solid line), and experimental spectrum of the phenoxyethyl acrylate (black solid line).

the C=O and C=C bonds (see scheme 1); the energy of this conformer (monomer B) is only 0.097 kcal mol⁻¹ higher than for monomer A. As can be seen in figure 4, interaction between C=O and C=CH₂ groups shifts the frequency of the $\nu\text{C(=O)-C(=CH}_2\text{)}$ mode from 1286 cm⁻¹ for monomer A to 1310 cm⁻¹ for monomer B. The implication is that the peaks at 1321 and 1286 cm⁻¹ are due to the stretching vibration $\nu\text{C(=O)-C(=CH}_2\text{)}$ of these two conformers. Assuming a Boltzmann distribution we calculated the spectrum as a sum of two components (assuming a weighting of 0.86 for monomer B). This yields much better agreement between the theoretical (blue curve in figure 4) and experimental data, indicating that both monomers are present in the monomer.

In figure 5 the theoretical spectrum calculated for an oligomer composed of four monomers (scheme 2) is compared to the experimental measurements on the polymer. The agreement is generally good, although some differences are evident. These are expected since the calculations were made for isolated molecules and the oligomer is approximated by only four monomers. Note that calculated spectra (not shown) for oligomers with only two or three repeat units gave worse agreement. Unfortunately, the required computational time increases with the degree of polymerization.

The decrease in the intensity of the C=C stretching bond (at 1637 cm⁻¹ for phenoxyethyl acrylate) provides a measure of the extent of the polymerization. However, since the experimental spectra were obtained using the attenuated total reflection technique, a direct comparison of the band intensities for the monomer and polymer cannot be made, since the materials differ in refractive index and thus penetration depth of the IR beam. Thus, we renormalized the intensity assuming that the integral intensities of the aromatic carbon stretching vibrations, at 1600 and 1588 cm⁻¹, are equal for the liquid and polymer sample (the phenyl ring is not involved in the polymerization reaction). The integral intensity ratios, $R = I_{\text{polymer}}/I_{\text{liquid}}$, are listed in table 1, showing that

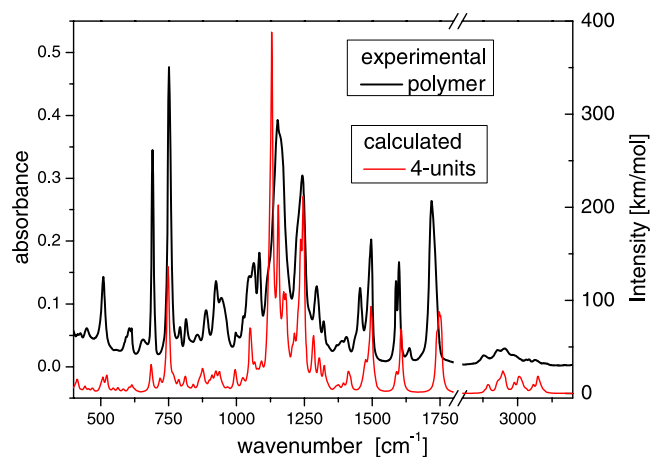


Figure 5. Calculated (red solid line) and experimental (black solid line) IR spectra of the polymer.

for moieties inactive during polymerization, the normalized intensities are equal: for the benzene ring CC vibrations (νCC at 1455 cm⁻¹ and γCC at 509 cm⁻¹), this ratio is very close to unity. For γCH benzene vibrations, at 752 and 691 cm⁻¹, the ratio is slightly higher but within the experimental error. The intensity ratios of the $\nu_{\text{as}}\text{C(H}_2\text{)-O-C(=O)}$ band at 1151 cm⁻¹ and the $\nu\text{C=O}$ band at 1719 cm⁻¹ are also unity, although for the polymer the peaks are much more asymmetrical than for the liquid. For the νCC band at 1496 cm⁻¹ there is a substantial increase in the ratio, but this is due to the overlapping δCH_2 vibration at 1487 cm⁻¹. The situation is similar for the overlapping $\nu_{\text{as}}\text{C}_{\text{ph}}\text{-O-C(H}_2\text{)}$ band at 1243 cm⁻¹ and the δCH_2 peak at 1220 cm⁻¹.

We can conclude that renormalization of the spectra allows the extent of the reaction to be quantified. The result is that ~60% of the double bonds reacted during polymerization at 1 GPa and 373 K. The decreased intensity in the polymer spectrum is seen for the C=C stretching vibration at 1637 cm⁻¹, as well as the bands at 1321, 1295, 852, and 656 cm⁻¹. All these bands arise from vibrations involving the unsaturated carbons (see table 1).

Interestingly, the IR band at 814 cm⁻¹ increases in intensity by more than a factor of three during the polymerization. Our calculations indicate that it corresponds to skeletal vibrations of the chain backbone. This result suggests that a significant degree of polymerization was achieved.

5. Conclusion

Polymerization of phenoxyethyl acrylate was induced by a hydrostatic pressure of 1 GPa and 373 K, yielding a polymer with a substantial molecular weight. The conversion was about 60%, which compares favorably to industrial scale polymerizations, which yield conversions for common plastics such as polyethylene, polypropylene, and polymethylmethacrylate in the range from 5 to 10%. The fragility, or sensitivity of the segmental dynamics to temperature, is lower for the polymer than for the monomer.

Table 1. Comparison of the calculated and experimental vibrational frequencies for the monomer and polymer.

| Frequencies (cm ⁻¹) | | | | |
|---------------------------------|--------------|---------|--|-------------------|
| Calculated liquid | Experimental | | Description ^a | Ratio |
| | Liquid | Polymer | | |
| 1732 | 1719.0 | 1716.7 | $\nu\text{C}=\text{O}$ | 1.00 |
| 1650 | 1637.3 | 1637.8 | $\nu\text{C}=\text{C}$ | 0.40 |
| 1609 | 1598.9 | 1599.0 | νCC (8a) | |
| 1590 | 1587.8 | 1588.2 | νCC (8b) | 1.00 ^b |
| 1496 | 1495.8 | 1496.7 | νCC (19a) + δCH_2 | 1.18 |
| 1487 | | | $\delta_s\text{CH}_2$ | |
| 1458 | 1455.5 | 1454.3 | νCC (19b) | 1.06 |
| 1423 | 1405.0 | 1406.1 | $\delta_w\text{CH}_2$ | |
| 1310 | 1321.2 | 1320.7 | $\nu\text{C}(=\text{O})-\text{C}(=\text{CH}_2) + \nu\text{C}(=\text{CH}_2)-\text{C}(\text{H}_3)$ (A) δCH (3) | 0.64 |
| 1286 | 1295.4 | — | $\nu\text{C}(=\text{O})-\text{C}(=\text{CH}_2) + \nu\text{C}(=\text{CH}_2)-\text{C}(\text{H}_3)$ (B) $\nu\text{C}(=\text{O})-\text{C}(-\text{CH}_2-)$ | |
| 1248 | 1243.1 | 1245.1 | $\nu_{\text{as}}\text{C}_{\text{ph}}-\text{O}-\text{C}(\text{H}_2)$ | 1.21 |
| 1211 | ~1220 | ~1220 | δCH_2 | |
| 1168 | 1151.4 | 1159.2 | $\nu_{\text{as}}\text{C}(\text{H}_2)-\text{O}-\text{C}(=\text{O})$ | 1.00 |
| 1095 | | | $\nu\text{O}-\text{C}(\text{H}_2) + \nu\text{C}(\text{H}_2)-\text{C}(\text{H}_2) + \delta\text{O}-\text{C}(\text{H}_2)-(\text{H}_2)$ | |
| 1080 | 1084.3 | 1085.1 | δCH (18b) | |
| 1048 | 1063.7 | 1067.3 | $\nu\text{O}-\text{C}(\text{H}_2) + \nu\text{C}(\text{H}_2)-\text{C}(\text{H}_2)$ | |
| 1030 | 1025.5 | 1026.0 | $\nu_s\text{C}_{\text{ph}}-\text{O}-\text{C}(\text{H}_2)$ | |
| 990 | — | 997.4 | νCC (13) | |
| 948 | 944.6 | 943.2 | $\delta_w=\text{CH}_2$ | |
| 928 | 924.3 | 925.9 | γCH (17a) | |
| 874 | 888.0 | 889.0 | γCH (17b) | |
| 853 | 851.6 | 856.4 | $\nu\text{C}(\text{H}_2)-\text{C}(\text{H}_2)-\text{O}-\text{C}(=\text{O})-\text{C}(\text{H}_3)$ skeletal | 3.75 |
| 812 | 814.4 | 813.9 | $\delta_r=\text{CH}_2$ | 0.35 |
| 803 | 792.0 | 791.0 | $\delta_t=\text{C}(\text{H}_2) + \gamma\text{C}(=\text{O})$ | |
| 748 | 751.6 | 752.4 | γCH (11) | 1.14 |
| 686 | 690.8 | 691.1 | γCC (4) | 1.09 |
| 634 | 656.0 | 652.9 | $\gamma\text{C}(=\text{O}) + \delta_t=\text{C}(\text{H}_2)$ | 0.39 |
| 614 | 613.4 | 613.3 | $\delta\text{C}_{\text{ph}}-\text{O}-\text{C}(\text{H}_2)-\text{C}(\text{H}_2)$ skeletal | |
| 597 | 592.4 | 592.1 | $\delta\text{C}=\text{O} + \nu\text{C}(=\text{O})-\text{C} + \nu\text{C}-\text{C}(\text{H}_3)$ | |
| 507 | 509.5 | 509.4 | γCC (16b) | 0.99 |

^a Atom description in figure 1; (A), (B)—monomer A and B; mode description: ν —stretching, δ —in-plane deformation, γ —out-of-plane deformation; δCH_2 : s—scissoring, t—twisting, r—rocking, w—wagging; s—symmetric, as—asymmetric; numbering of benzene ring vibration according to Wilson.

^b Peaks chosen for comparison of the experimental spectra.

This unusual property may be related to the complicated geometry of the polymer, as revealed by DFT calculations.

Acknowledgments

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