2,5-Diphenyl-3,4-bis[*p*-(phenylethynyl)phenyl]cyclopentadienone and product of its Diels—Alder homocondensation

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A new monomer of the ABA type, 2,5-diphenyl-3,4-bis[*p*-(phenylethynyl)phenyl]-cyclopentadienone, was synthesized. The Diels—Alder homocondensation of the monomer resulted in a highly branched polyphenylene (M_w = 160000), readily soluble in organic solvents. The polymer obtained is thermally stable up to 600 °C (in argon atmosphere) and has a glass transition of 280 °C. The structure of the monomer and polymer was confirmed by ^{1}H NMR, ^{13}C NMR, IR Fourier, and Raman Fourier spectroscopy.

Key words: 2,5-diphenyl-3,4-bis[*p*-(phenylethynyl)phenyl]cyclopentadienone, 4,4'-bis-(phenylethynyl)benzil, homocondensation of monomers, Diels—Alder reaction, highly branched polyphenylene, differential scanning calorimetry, thermogravimetric analysis.

Currently, monomers of the ABA type, whose molecules contain fragments A and B, capable of entering into chemical reactions, attract the attention of investigators as initial compounds for the synthesis of highly branched polymers (HBPs) that are of interest as spherical multifunctional macromonomers and agents for controlling the rheology of polymer melts.[1] Among various HBPs obtained by homocondensation of monomers of the ABA type, of particular interest are highly branched oilgophenylenes and polyphenylenes, combining high thermal stability and solubility in various solvents.[1–3]

In this work we report the synthesis of a previously unknown monomer of the ABA type, 2,5-diphenyl-3,4-bis[*p*-(phenylethynyl)phenyl]cyclopentadienone (**1**).

Monomer **1** was synthesized according to Scheme 1. Reaction of 4,4'-bis(phenylethynyl)benzil,[4] used as the initial compound, with an equimolar amount of 1,3-diphenylacetone, conducted following the known procedures,[5,6] in butanol resulted in compound **1** in 88% yield.

The structure of product **1** was confirmed by elemental analysis, ^{1}H and ^{13}C NMR, IR Fourier, and

Scheme 1

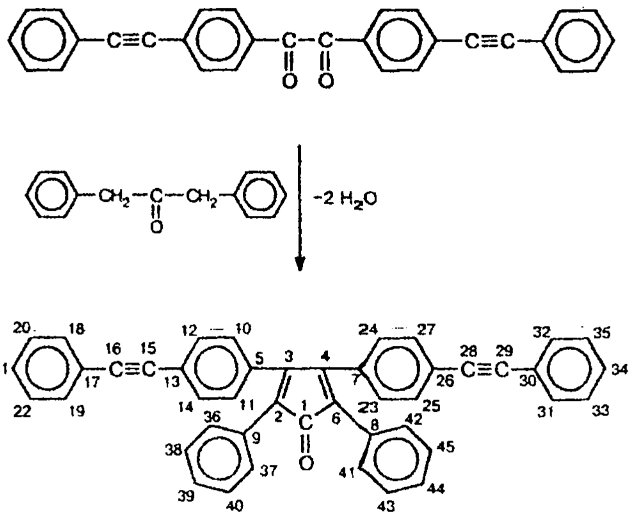

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Table 1. Parameters of ^1H and ^{13}C NMR spectra (in $CDCl_3$) of 2,5-diphenyl-3,4-bis[*p*-(phenylethynyl)phenyl]cyclopentadienone (**1**)[a]

δ ^1H (*J*/Hz)	Atom	δ ^{13}C		Atom	δ ^{13}C	
		found	calculated		found	calculated
7.40—7.60 (m, 4 H);	C(1)^b	199.62	—	C(16, 29)^b	88.91	91.00
7.36 (d, 4 H, H(12, 27),	C(2, 6)^b	125.60	126.40	C(17, 30)^b	123.41	122.30
H(14, 25), *J* = 8.1);	C(3, 4)^b	153.13	151.50	C(18, 19, 31, 32)	131.48	132.10
7.31—7.34 (m, 6 H);	C(5, 7)^b	130.24	131.60	C(20, 22, 33, 35)	128.39	128.10
7.20—7.30 (m, 10 H);	C(8, 9)^b	132.63	133.90	C(21, 34)	129.33	128.20
6.93 (d, 4 H, H(10, 24),	C(10, 24)	127.61	125.80	C(36, 37, 41, 42)	128.05	126.20
H(11, 23), *J* = 8.1)	C(12, 27)	131.17	132.00	C(38, 40, 43, 45)	130.01	128.45
	C(13, 26)^b	122.75	121.50	C(39, 44)	128.27	127.70
	C(15, 28)^b	90.80	91.00			

[a] The numbering of atoms is shown in Scheme 1.

[b] The signal of quaternary carbon atom.

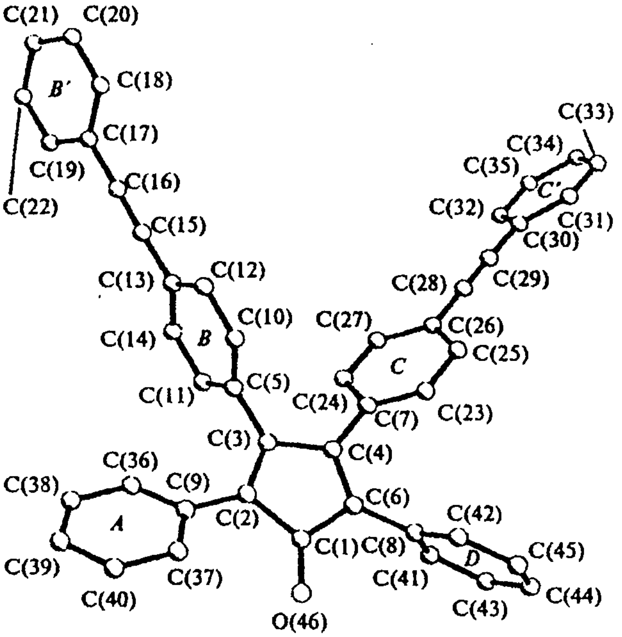


Fig. 1. A model of the structure of the 2,5-diphenyl-3,4-bis[*p*-(phenylethynyl)phenyl]cyclopentadienone molecule (**1**) in the equilibrium conformation obtained after geometry optimization by the AM1 method.

Raman Fourier spectroscopy (Table 1). A strong absorption band with a maximum near 1710 cm^{-1}, characteristic of the stretching vibrations of the CO group of cyclopentadienone,[5] and a weak band in the region 2210 cm^{-1} corresponding to the acetylene group are observed in the IR spectrum of compound **1**. The Raman spectrum consists of a weak band in the region 1710 cm^{-1} and a strong band near 2210 cm^{-1} that can be assigned to the stretching vibrations of carbonyl groups of the cyclopentadienone and acetylene fragment, respectively.

Three groups of well resolved signals at δ 7.40—7.60, 7.31—7.34, and 7.20—7.30 are observed in the ^1H NMR spectrum of compound **1** (see Table 1) in addition to the signals of the AA′BB′-system at δ 7.36 (H(12, 27), H(14, 25)) and δ 6.93 (H(10, 24), H(11, 23)) corresponding to the aromatic protons.

The presence of the low-field signal at δ 199.5 characteristic of the C(1) atom of the carbonyl group and two high-field signals at δ 90.80 and 88.91 corresponding to two inequivalent atoms (C(15) and C(16)) of the ethynyl fragment is a characteristic feature of the ^{13}C NMR spectrum of compound **1**. In addition to the three characteristic signals, 14 intense signals assigned to 14 expected inequivalent carbon atoms are also observed in the ^{13}C NMR spectra in the region δ 153—122 (see Table 1). The chemical shifts for compound **1** were also calculated by the additive scheme using the increments for substituted benzenes.[7] All calculated chemical shifts coincide with those observed in the ^{13}C NMR spectrum with an accuracy of ±2 ppm.

Since it is impossible to establish the spatial arrangement of the phenyl rings in the molecule of compound **1** using NMR spectra, we studied its molecular structure by conformational analysis. The geometry of the equilibrium conformation of compound **1** was estimated by the AM1 semiempirical quantum-chemical method,[8] which is the most convenient method for calculating conjugated π-systems and heterocyclic compounds. The calculations showed that the benzene rings bonded to the central planar five-membered cycle of molecule **1** (Fig. 1) deviate out of the plane of this cycle. The values of corresponding torsion angles characterizing the angles of rotation of the benzene rings about the five-membered cycle are listed in Table 2. Noteworthy is that, according to calculations, two diametrically opposite benzene rings (*B* and *D*) are turned through angles close to 90° with respect to the plane of the five-membered cycle, whereas the other two diametrically opposite benzene rings (*A* and *C*) are turned through appreciably smaller angles. We believe that such an asymmetric "propeller-type" conformation confirms the presence of conjugation in the molecule, since, on the one hand, the benzene rings and the five-membered cycle form a common aromatic system, the former tending to be retained in the plane of the cycle, and, on

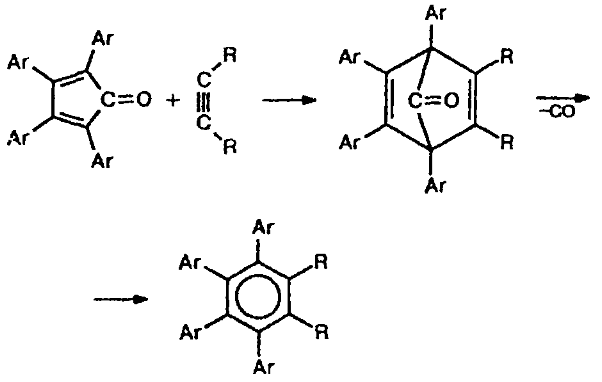
Table 2. Torsion angles (φ) in molecule **1**

Cycle	Angle	φ/deg
A	C(3)—C(2)—C(9)—C(36)	33.1
D	C(4)—C(6)—C(8)—C(41)	−79.6
B	C(2)—C(3)—C(5)—C(10)	91.3
C	C(6)—C(4)—C(7)—C(23)	−46.3

the other hand, they have to deviate out of this plane because of steric hindrances.

It is known that tetraarylcyclopentadienones enter into the Diels—Alder reaction with acetylenesthe,[5,6,9–12] following Scheme 2.

Scheme 2



We used this reaction to synthesize a highly branched polyphenylene based on compound **1** (Scheme 3).

Analysis of Scheme 3 shows that each of the oligomeric products that formed contains one unreacted cyclopentadienone group and $x + 1$ unreacted phenylethynyl groups (x is the degree of polymerization), which is in agreement with the published data.[13,14]

Homocondensation of compound **1** was conducted in refluxing 1,2,4-trichlorobenzene over a period of 7 h; the increase in duration of the reaction was accompanied by the precipitation of insoluble residue, which is most likely due to the entrance of acetylene groups into trimerization reactions resulting in "cross-linking" of the polymer. The polymer obtained is soluble in organic solvents (CH_2Cl_2, $CHCl_3$, THF, DMF, and DMSO). The number-average molecular weight of the polymer ($\overline{M}_w$) determined by sedimentation in an ultracentrifuge was 160000. At the same time, the specimen contained a small amount (~10%) of a polymer with a molecular weight of about 1500000. The rather large molecular weight and the presence of high-molecular-weight components confirm the occurrence of different (star-shaped, dendritic, statistical, *etc.*) branching processes that are possible in the case of homocondensation of monomers of the ABA type.[13]

The structure of the polymer obtained was confirmed by spectroscopic data. An absorption maximum at ν 2215 cm^{-1} corresponding to acetylene groups, the number of which at the periphery of the branched macromolecule is very large, is observed in its IR spectrum (Fig. 2). No absorption band corresponding to the carbonyl group of cyclopentadienone residue is observed, which is likely due to the high degree of polymerization of the product.

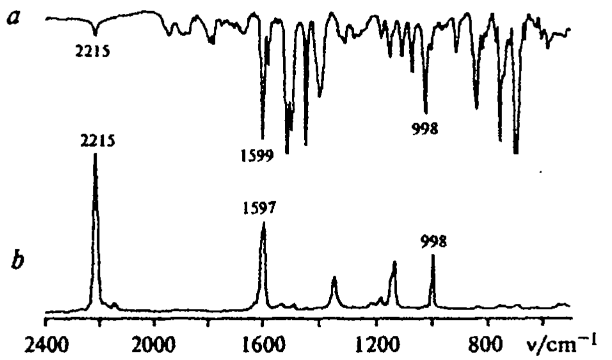


Fig. 2. Total vibrational spectrum of highly branched polymer based on 2,5-diphenyl-3,4-bis[*p*-(phenylethynyl)phenyl]cyclopentadienone: *a*, IR spectrum; *b*, Raman spectrum.

A broad peak in the region δ 7.00—8.50 is observed in the ^{1}H NMR spectrum of the polymer. This broadening can be a result of the presence of various isomers. More conclusive spectroscopic proofs of the structure of the polymer were obtained by ^{13}C NMR spectroscopy.

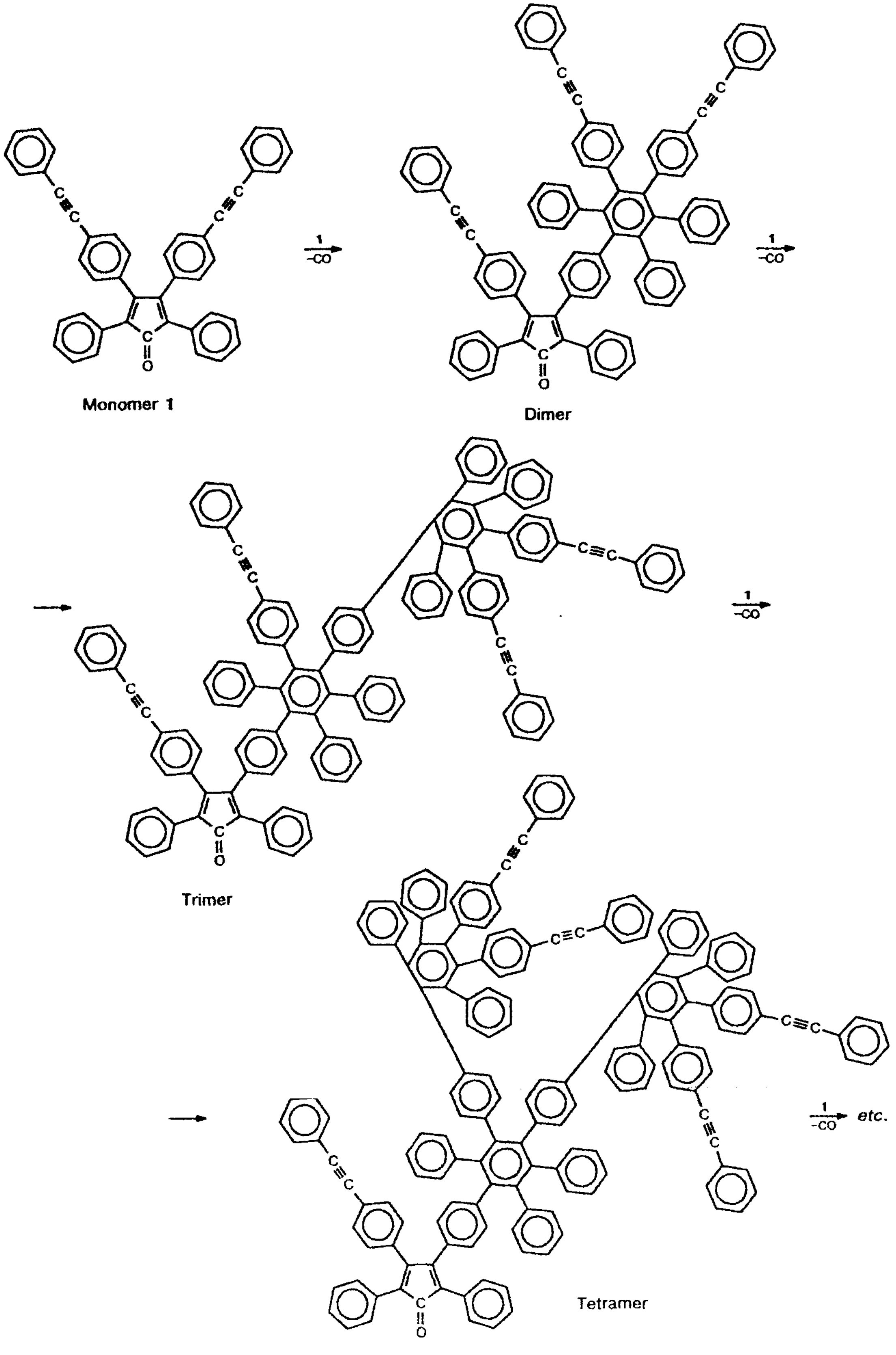
Analysis of the ^{13}C NMR spectrum showed that homocondensation of compound **1** leads to the appearance of signals in the region δ 136.0—141.0 characteristic of a completely phenylated benzene ring and to considerable decrease in the intensity of the signal at δ 199.62 (compared to that of the signal in the spectrum of monomer **1**) corresponding to the carbonyl group of the cyclopentadienone residue (this signal was not detected). The signals at δ 88.98 and 89.78 correspond to two inequivalent carbon atoms in a peripheral acetylene fragment of the polymer.

Thermal properties of compound **1** and the highly branched polymer synthesized on its basis were studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) in the temperature range 25—650 °C.

The DSC curves of model tetraphenylcyclopentadienone (*a*), compound **1** (*b*), and the polymer (*c*) are shown in Fig. 3. A narrow melting endotherm with a maximum near 260 °C and a narrow triple-bond cross-linking exotherm with a maximum at 393 °C can be seen in the DSC curve shown in Fig. 3, *b*. The DSC curve shown in Fig. 3, *c* indicates a glass transition of the polymer near 280 °C and a broad triple bond cross-linking exotherm with a maximum at 380 °C.

The results of thermogravimetric analysis indicate an excellent thermal stability of the highly branched polymer. The 10% weight loss temperature in an argon atmosphere is 594 °C. As can be seen, the thermal stability of the polymer is higher than that of linear analogs and corresponding model compounds.[1,2]

Scheme 3



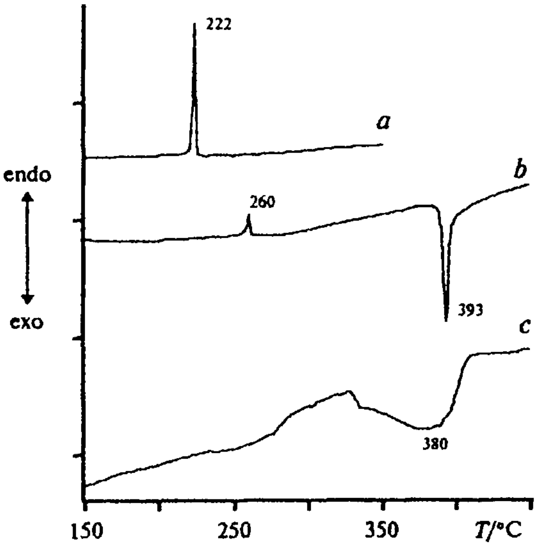


Fig. 3. DSC curves of tetraphenylcyclopentadienone (*a*), 2,5-diphenyl-3,4-bis[*p*-(phenylethynyl)phenyl]cyclopentadienone (**1**) (*b*), and highly branched polymer based on compound **1** (*c*).

Thus, we synthesized a highly branched polyphenylene based on monomer **1** and containing active peripheral phenylethynyl functional groups that can be replaced by various substituents. Replacement of end functional groups accompanied by substantial changes in the solubility, glass transition temperature, and other parameters would make it possible to perform targeted modification of the characteristics of branched polymers.

Experimental

Initial compounds and solvents were purified following the known procedures.[4]

^{1}H and ^{13}C NMR spectra (in $CHCl_3$) were recorded on a Bruker AMX-400 spectrometer operating at 400.13 and 100.61 MHz, respectively. IR and Raman spectra were recorded on a Perkin—Elmer-1720 X IR Fourier spectrophotometer equipped with an Nd:YAG laser (the Raman excitation wavelength was 1064 nm). The dynamics of the transformations was monitored by TGA on a Perkin—Elmer TGA-7 instrument at a heating rate of 10 deg min^{-1} and by DSC on a Perkin—Elmer DSK-4 instrument at a heating rate of 20 °C min^{-1}.

The molecular weight of the polymer specimen under study was determined by sedimentation analysis by the meniscus depletion sedimentation equilibrium method.[15] The experiments were carried out on an MOM-3180 (Hungary) analytical ultracentrifuge using double-sector cells. One sector was filled with the solvent and the other sector was filled with polymer solutions of different concentrations in the range 0.1—0.5 g L^{-1}. The rotor speed (10—15000 rev min^{-1}) was chosen in such a way that the gradient concentration curve intersects the meniscus at an angle of ~45°, the rotor temperature was 25±0.1 °C, and $CHCl_3$ was used as the solvent. Changes in the gradient curve with time were detected using Philpot—Swensson optics. To determine the true number-average molecular weight ($\bar{M}_w^{\rm true}$), the apparent weight-average molecular weights ($\bar{M}_w^{\rm app}$) calculated at four finite concentrations were extrapolated to zero concentration. The partial specific volume (V = 0.796 mL g^{-1}) and density (1.4849 g cm^{-3}) of chloroform were determined pycnometrically.

2,5-Diphenyl-3,4-bis[*p*-(phenylethynyl)phenyl]cyclopentadienone (1). 4,4′-Bis(phenylethynyl)benzil (2.05 g, 5 mmol), diphenylacetone (1.31 g, 6.25 mmol), and 70 mL of *n*-buthanol were placed in a three-neck flask equipped with a stirrer, a reflux condenser, and a thermometer. The reaction mixture was heated to boiling and Triton B (0.57 mL, a 40% solution in MeOH) was added as catalyst. The solution immediately turned violet. After 1 h, the same amount of Triton B was added and the mixture was refluxed for an additional 3 h and cooled to 20 °C. The residue that precipitated was filtered off, thoroughly washed with cold EtOH, and dried *in vacuo* at 80 °C (10 h) to give 2.57 g (88%) of compound **1**, m.p. 261—262 °C (from Bu^{n}OH). Found (%): C, 92.41; H, 4.93. $C_{45}H_{28}O$. Calculated (%): C, 92.50; H, 4.82.

Polymer. Compound **1** (1.169 g, 2 mmol) and 3.3 mL of 1,2,4-trichlorobenzene were placed in a three-neck flask equipped with a stirrer, an argon inlet, and a reflux condenser. The reaction mixture was refluxed for 7 h, then cooled to 20 °C, and poured into MeOH (150 mL). The residue that precipitated was filtered off, then a fresh portion of methanol was added to the precipitate, and the solution was refluxed for 3 h; then the polymer precipitate was filtered off and dried *in vacuo* at 100 °C (10 h). The yield was 1.01 g (86%). ^{13}C NMR ($CDCl_3$, δ): 88.98, 89.78 ($C\equiv C$); 120.02 (C arom.); 123.48 (C arom.); 125.16 (C arom.); 126.57 (C arom.); 128.17 (C arom.); 130.07 (C arom.); 131.41 (C arom.); 136.75 (C arom.); 140.52 (C arom.). The vibrational spectra and DSC curves of the polymer obtained are shown in Figs. 2 and 3, respectively.

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