

# Copolymerization of benzoquinone with norbornene

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## Abstract

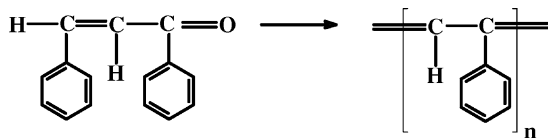
For the first time, the conjugated dicarbonyl compound benzoquinone has been copolymerized with the strained cyclo-olefin norbornene using catalytic amounts of the Friedel-Crafts metathesis catalytic system  $\text{WOCl}_4 + \text{AlCl}_3$ . All analyses reveal that the products consist of conjugated blocks originating from benzoquinone connected with spacers originating from norbornene. The products are soluble in benzene, toluene, chlorobenzene, etc. but possess properties of the conjugated polymers. They have been synthesized via a very simple one-pot procedure.

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**Keywords:** Copolymerization; Conjugated diketones; Strained cyclo-olefins; Conjugated polymers; Metathesis catalytic systems

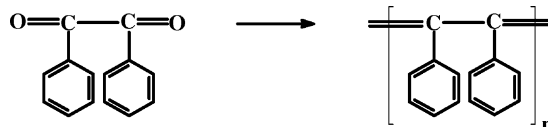
## 1. Introduction

Our studies have shown Friedel-Crafts metathesis catalytic systems ( $\text{WCl}_6 + \text{AlCl}_3$ ,  $\text{WOCl}_4 + \text{AlCl}_3$ ,  $\text{TiCl}_3 + \text{AlCl}_3$ ,  $\text{WOCl}_4 + \text{GaBr}_3$ ) to be versatile systems provoking polymerization of  $\alpha,\beta$ -unsaturated carbonyl compounds (carbonyl–olefin exchange reaction; Scheme 1) [1], reductive coupling of con-



Scheme 1.

jugated dicarbonyl compounds [2] (Scheme 2), and co-polymerization of conjugated dicarbonyl compounds with strained cyclo-olefins [3] (Scheme 3).



Scheme 2.

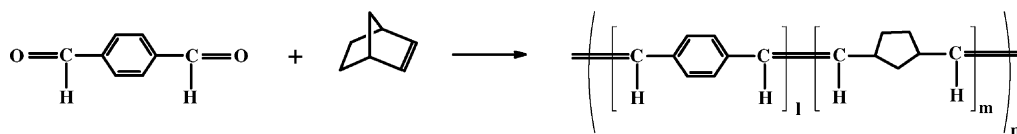
The homopolymerizations result in conjugated polymers whereas the copolymerization yields block copolymers comprising conjugated rigid segments. Like the olefin, metathesis carbonyl–olefin exchange reaction and reductive coupling of carbonyl compounds are double-bond formation reactions. A hypothesis about the carbene mechanism of these reactions was launched [4].

Being a representative of the conjugated dicarbonyl compounds benzoquinone is expected to copolymerize with strained cyclo-olefins under the influence of Friedel-Crafts metathesis catalytic systems.

This communication reports on the first results from our attempts to copolymerize benzoquinone with norbornene.

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Scheme 3.

## 2. Experimental

### 2.1. Materials

Benzoquinone (Fluka) was sublimed before use. Norbornene (Fluka) was distilled before use. Chlorobenzene (p.a. from Loba Chemie) was dried over  $\text{CaH}_2$  and distilled before use. Tungsten oxychloride and aluminum chloride (Merk) were used as received.

### 2.2. Methods

IR spectra were recorded from KBr pellets on a Bruker Vector 22 spectrophotometer. Electronic spectra were recorded in chloroform on a Specord spectrophotometer (Carl Zeiss-Jena).  $^1\text{H}$  NMR spectra were recorded in  $\text{CDCl}_3$  at room temperature on a Bruker WM 250 spectrometer. ESR spectra were recorded in air on a JES-3BX (JEOL) apparatus using diphenylpicrylhydrazyl as a standard. GPC measurements were taken on a Waters 244 apparatus with refractometric (RI) and UV–VIS detectors; 100, 100, and 500 Å ultrastyrigel columns at 25 °C in THF; rate of elution 0.8 ml/min. Polystyrene calibration was used.

Electrical conductivities were measured on pressed pellets by two-points probe on a Keithley 617 electrometer. Doping with iodine was performed at ambient temperature for several hours in a dessiccator containing iodine in an open dish. Then the samples were evacuated till constant weight.

### 2.3. Copolymerization

The reaction was carried out using Schlenk technique in a reaction flask, supplied with a reflux condenser and a magnetic stirrer.

A mixture of 0.6 g of  $\text{WOCl}_4$  (1.8 mmol), 0.8 g of  $\text{AlCl}_3$  (6 mmol) and 25 ml of chlorobenzene was

aged for 15 min at room temperature. Solution of 1.3 g of benzoquinone (12 mmol) and 2.2 g of norbornene (23 mmol) in 25 ml of chlorobenzene were added to the reaction mixture. The reaction vessel was put into a pre-heated bath at 90 °C. The mixture was kept for 4 h at this temperature under vigorous stirring. Then it was cooled to room temperature and 0.5 ml HCl (15%) was added and stirred for 15 min. Then the reaction mixture was poured into 300 ml of ethanol, left overnight and filtered. All the solvents were removed under reduced pressure. The residue was dissolved in chloroform and washed with HCl and with water until neutral. The mixture was filtered and 50 ml of alcohol were added. A part of the chloroform was evaporated. The first precipitate containing inorganics was filtered off. The removal of the inorganics was repeated. Finally, all the solvents were removed and the products were dried under reduced pressure. Yield was 3 g.

## 3. Results and discussion

We have shown previously that the conjugated dicarbonyl compound terephthalaldehyde is able to copolymerize with the strained cyclo-olefin norbornene under the influence of a Friedel-Crafts metathesis catalytic system.

The product is a block copolymer composed of conjugated poly(*p*-phenylenevinylene) segments, originating from terephthalaldehyde and spacer blocks, originating from norbornene [3] (Scheme 3).

The main points in this study are:

1. It is difficult to control the spacer structure because norbornene can polymerize according to different mechanisms (via metathesis or Ziegler-Natta polymerization) [5]. Though, the conjugated blocks are short, the product possesses properties characteristic of the conjugated polymers which is in agreement with the investigations of Schopov and Sinigersky [6].

2. Regardless to the fact, that the polymerization of the terephthalaldehyde resembles McMurry reaction [6] (carbon–carbon double-bond formation reaction starting from carbonyl compounds), most probably the mechanisms of these two reactions are different, because we do not use any reducing agent. Even the ratio monomer:catalyst >1:1 is much higher than the ratio monomer:reducing agent <1:2 used for McMurry reaction [7].
3. We propose a very simple one-pot procedure for the synthesis of soluble and processable copolymers

with valuable properties like electrical conductivity, photoluminescence, etc. due to the conjugated blocks in the polymer chain.

As we have shown, the polymerization of conjugated dicarbonyl compounds under the influence of Friedel-Crafts metathesis catalytic systems yields conjugated structures. The conjugated diketone benzoquinone was chosen as a monomer for the present investigations, because we expected to synthesize block copolymers comprising conjugated blocks with a novel-quinoid structure (Scheme 4).

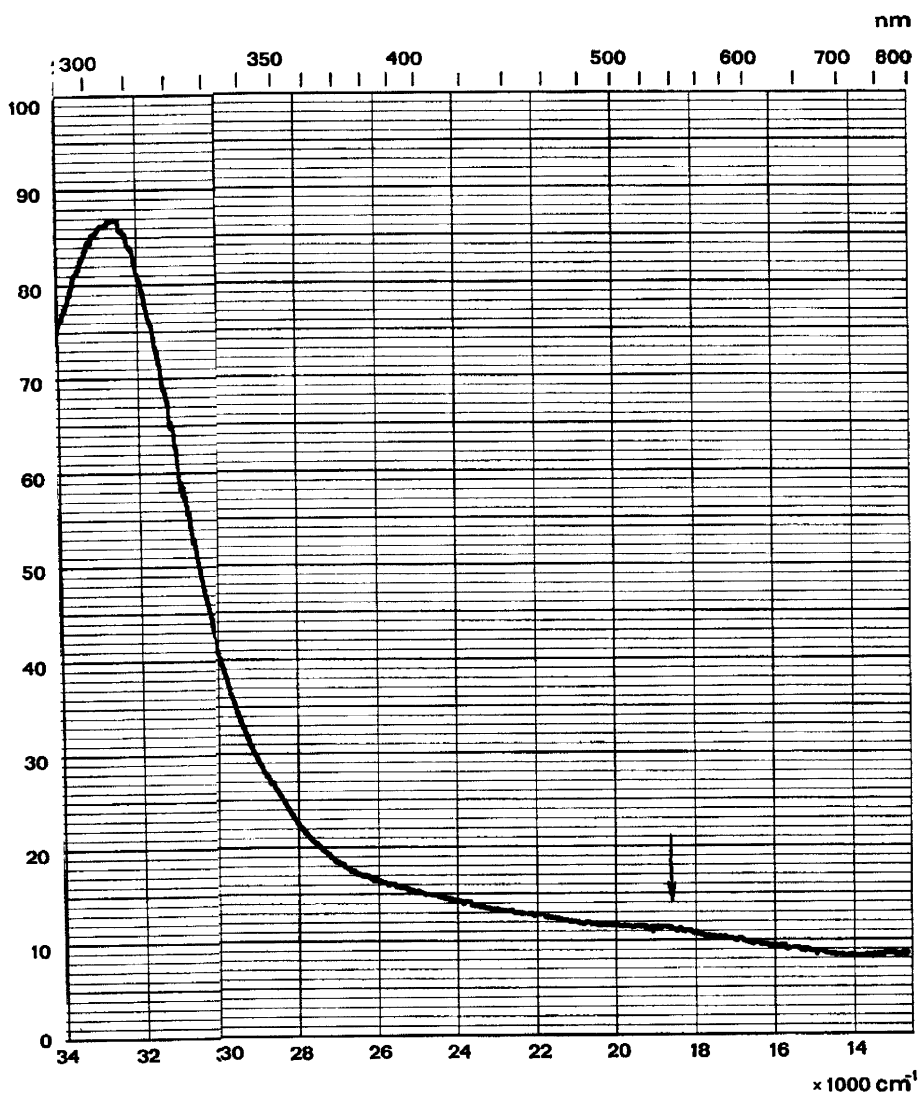
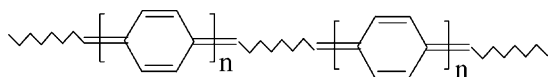


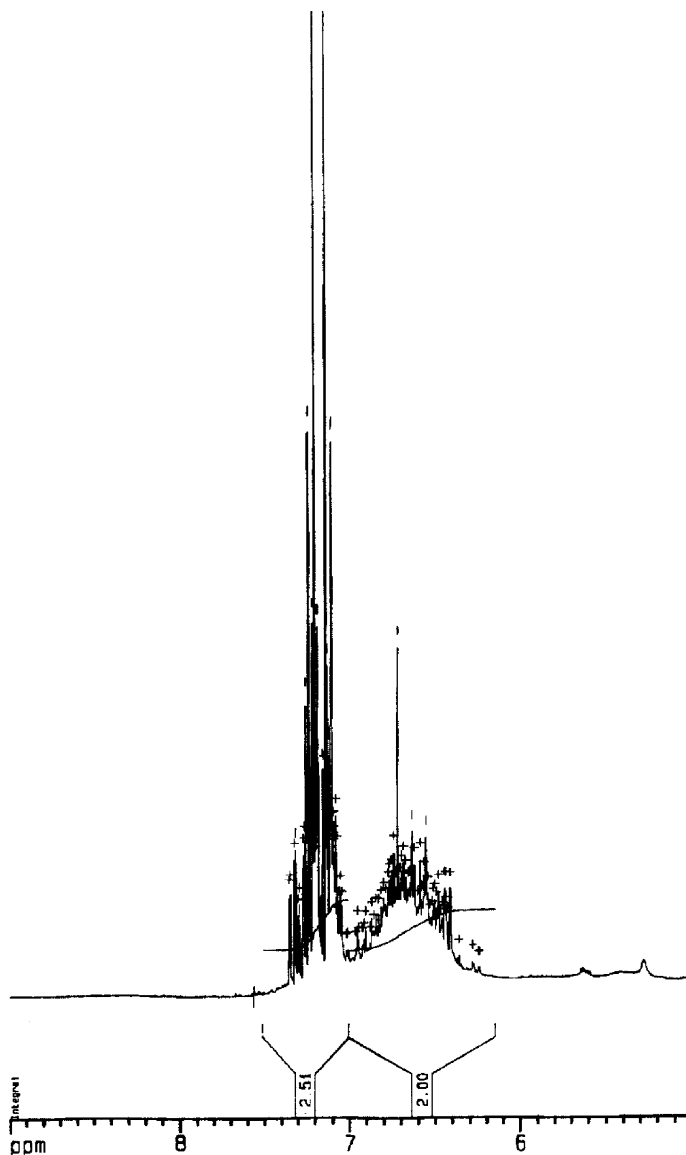
Fig. 1. UV-VIS spectrum of the product.



Scheme 4.

We started our experiments using the system  $\text{WOCl}_4 + \text{AlCl}_3$ . This system was used in catalytic amounts for performing the carbonyl–olefin exchange reaction [4]. Fortunately, it is able to transform benzo-

quinone and norbornene into oligomer products. The yield and the molecular weights of the resulting products depend on the molecular ratios, monomer:catalyst and catalyst:co-catalyst; as well as on the temperature; aging time of the catalytic system, etc. The experimental conditions, represented in this communication show that high yields of the new products can be achieved using only 1 mol of the catalyst per 12 carbonyl groups. This ratio is an unprecedented result for

Fig. 2.  $^1\text{H}$  NMR spectrum of the product.

the formation of carbon–carbon double bonds from carbonyl compounds. Catalytic amounts of the transition metal reducing agent were achieved only by using chlorosilanes as additives [8].

The products obtained are soluble in benzene, toluene, chloroform, etc. They are colored. The main peak in the UV–VIS spectrum is at 310 nm. Weak peak appears at 550 nm (Fig. 1). The latter wavelength was chosen for the UV–VIS detector of the GPC apparatus. The GPC analyses show that the reaction product consists of oligomer products absorbing at 550 nm. No products, which do not absorb at this wavelength are detected with the RI-detector. The IR spectra of the products have absorbancy peaks corresponding to the aliphatic C–H vibrations. These facts show that the oligomers are single species whose molecules are composed of conjugated (originating from benzoquinone) and non-conjugated (originating from norbornene) structures. The molecular weights of the oligomers, determined by GPC are in the range between 1200 and 70. These values are irrelevant since molecular weights of the monomers are higher than 70.

At the moment, we are cautious to describe the molecular structure of the products because all spectral analyses are too complicated. For example, two sets of absorbances above 5.5 ppm (around 7.2 and 6.6 ppm) are observed in the  $^1\text{H}$  NMR spectra (Fig. 2). This reveals that the possibility of isomerization of the quinoid structure into benzoid one should be considered. Nevertheless, the product has physical properties characteristic for conjugated polymers. Doping with iodine led to enhancement in the electrical conductivity (from  $10^{-13}$  to  $10^{-9}$  S/sm) of the product. It itself is paramagnetic ( $10^{16}$  sp/g,  $g \sim 2$ ). The most interesting fact observed is that this product is soluble in nematic liquid crystal eutectic mixture of cyanobiphenyls LC-807–“NIOPIK” Russia with

positive dielectric anisotropy ( $\Delta\epsilon > 0$ ). The temperature of the nematic–isotropic transition of the mixture decreases but the mixture still keeps its nematic liquid–crystalline alignment. Both components can be oriented in electric field.

#### 4. Conclusion

We succeeded for the first time in copolymerizing the conjugated diketone benzoquinone with the strained cyclo-olefin norbornene using catalytic amounts of the Friedel-Crafts metathesis catalytic system  $\text{WOCl}_4 + \text{AlCl}_3$ . The synthesis itself is a very simple one-pot procedure. The reaction product possesses physical properties characteristic for the conjugated polymers. Further studies should be done in order to interpret precisely the molecular structure of the products and to gain an idea about the mechanism of this reaction.

#### Acknowledgements

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