

Copolymerization of a conjugated dicarbonyl compound with a strained cycloolefin mediated by a metathesis catalytic system

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Abstract

A very simple one-pot synthesis of a copolymer consisting of conjugated fragments connected by aliphatic segments is presented. The copolymerization of terephthalaldehyde with norbornene proceeds under the influence of the binary system $\text{TiCl}_3 + \text{AlCl}_3$. The products are oligomers with monomodal broad molecular weight distribution (dispersity = 2.8; $\overline{M}_w = 3900$). The IR bands are assigned to aromatic, olefinic and aliphatic C-H vibrations. The absorption in the visible range reveals conjugated blocks in the backbone. The products are soluble in benzene, toluene, chloroform, etc. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Carbonyl-olefin exchange reaction; Reductive coupling of carbonyl compounds; Olefin metathesis; Transition metal halides; Copolymerization; Conjugated polymers

1. Introduction

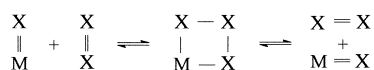
We have shown previously that α, β -unsaturated carbonyl compounds can polymerize under the influence of transition metal halides (WCl_6 , MoCl_5), transition metal oxohalides (WOCl_4) and binary systems ($\text{WCl}_6 + \text{AlCl}_3$, $\text{WOCl}_4 + \text{AlCl}_3$) [1,2]. The polymer formation was described in terms of a redistribution of atoms involving *oxo*- and carbene-transition metal complex intermediates and four-membered

metallacycle transition states [3,4] (Scheme 1).

These processes are representatives of a much larger family of [2 + 2] metathesis reactions between multiply bonded compounds [5].

We launched this hypothesis in order to explain the experimental results, i.e., yield of oligomer and low molecular weight products from the polymerization of 1,2,3,3-tetraphenylprop-2-en-1-one [4]. According to this hypothesis, the overall polymerization processes can be visualized in terms of the several reactions: carbonyl-olefin exchange reaction (COER) [1] (Scheme 2), olefin metathesis (OM) [5] (Scheme 3); reductive coupling (RC) of carbonyl com-

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X = C, O, M

M is a transition metal.

Scheme 1.

pounds [6] accompanied by evolution of molecular oxygen (Scheme 4); suggesting that these three reactions run simultaneously.

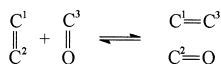
Secondary reactions of the products, involving internal double bonds, may also occur. All the reactions mentioned above are double bond formation reactions. The identification of tetraphenylethylene, benzophenone and molecular oxygen as low molecular products supports this hypothesis [3]. Another test would be the structure of the oligomer products, though not in the case of 1,2,3,3-tetraphenylprop-2-en-1-one polymerization, because any of the above reactions results in the formation of polydiphenylacetylene-repeating units. A way to round this problem is to study the reactions between two different molecules, one containing the carbonyl and the other the olefinic functionalities, then each reaction will result in different structure.

The present paper reports our recent investigations on the copolymerization of a conjugated dicarbonyl compound with a strained cycloolefin, namely terephthalaldehyde (TA) with norbornene (NB). The main reason for choosing this monomers was that their structures are easy to distinguish.

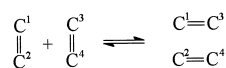
2. Experimental

2.1. Materials

Terephthalaldehyde (Fluka), norbornene (Fluka), titanium(III) chloride (Aldrich) and alu-



Scheme 2.



Scheme 3.

minium chloride (Merck) were used as received. Chlorobenzene (p.a. from Loba Chemie) was dried over CaH₂ and distilled before use.

2.2. Methods

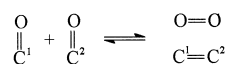
IR spectra were recorded from KBr pellets on a Perkin-Elmer 1600 FTIR spectrophotometer. Electronic spectra were recorded on a Specord spectrophotometer (Carl Zeiss-Jena) in chloroform. ¹H NMR spectra were recorded in CDCl₃ at room temperature on a Bruker WM 250 spectrometer. Luminescent spectra were recorded in chloroform on a Perkin-Elmer MPF-44 spectrofluorimeter. ESR spectra were recorded in air using JES-3BX (Jeol) apparatus with biphenylpicrylhydrazyl as a standard. GPC measurements were taken on a Waters 244 apparatus having refractometric (RI) and UV detector; 100, 100, 500 Å columns; at 45°C in THF; rate of elution 0.8 ml/min. Molecular weights \bar{M}_n were also determined on a Knauer vapor pressure osmometer.

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

2.3. Copolymerization

The reaction was carried out in a two-necked flask equipped with an inert gas inlet (nitrogen), a reflux condenser and a magnetic stirrer.

Terephthalaldehyde (1 g), norbornene (1 g), titanium(III) chloride (1 g), and aluminium



Scheme 4.

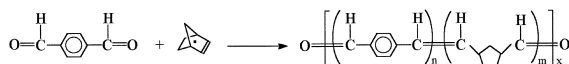
chloride (0.8 g) were mixed in 20-ml chlorobenzene at room temperature. The reaction vessel was put into a pre-heated bath at 130°C. The mixture was kept for 24 h at this temperature under vigorous stirring. Then it was cooled to room temperature and methanol (0.5 ml) was added. After filtration over a layer of Al₂O₃ and the elution of the filter cake with toluene, the solution was concentrated under reduced pressure and precipitated in methanol. The precipitate was dissolved in chloroform, the solution was filtered, concentrated and precipitated in methanol. This procedure was repeated several times until no product insoluble in chloroform (inorganic residue) was observed. After the final precipitation, the organic residue was dried in vacuo at room temperature. Yield ca. 1.7 g, ca. 95%. $\overline{M}_n = 3600$ (determined osmotically); $\overline{M}_n/\overline{M}_w = 2.6$ (determined by GPC).

3. Results and discussion

The polymerization of TA via RC coupling results in the formation of poly-(*p*-phenylenevinylene) (PPV) [7–9], which has gained attention in the recent years mainly as an acting element in light-emitting devices [10]. Furthermore, NB is one of the most investigated monomers for ring-opening metathesis polymerization (ROMP) [5]. If these monomers undergo the conversions discussed above, the processes may be represented as shown in Scheme 5.

There are several possibilities.

(1) $m = 0$ or $n = 0$; $x \neq 0$. This is the case when the two monomers homopolymerize. RC and ROMP proceed independently. The molecular weight distribution of the products determined by GPC should be bimodal according to RI detector and monomodal according to the UV (at 254 nm) detector.



Scheme 5.

(2) $n > 1$, $m > 1$; $x = 1$. The product is a diblock copolymer. Its electronic spectra should have a maximum at ~ 400 nm corresponding to the effective length of conjugation for PPV [11]. In this case, RC and ROMP proceed consequently, the shift from RC to ROMP or vice versa occurs via COER.

(3) $m = n = 1$; $x > 1$. The product is an alternating copolymer. It should not absorb in the visible range. In this case, only COER takes place.

(4) $m \neq n$; $x > 1$. The product is a random copolymer. It should absorb in the visible range. In this case, all three reactions under discussion run simultaneously.

It is well-known that NB can be polymerized using the monocomponent catalyst WCl₆ [5]. However, the transition metal halides (WCl₆, MoCl₅, TiCl₄ and TiCl₃) failed to induce copolymerization of NB and TA. Two-component system (transition metal halide + Lewis acid) was therefore examined. It is a representative of the so-called Friedel-Crafts' two-component systems for OM [5]. Such a system (WCl₆ + AlCl₃) gives better results from COER [2]. In addition, we succeeded in transforming benzyl into polydiphenylacetylene using WCl₆ + AlCl₃ [12]. This is the first case in which a non-reduced transition metal reagent has been used for RC of a carbonyl compound.

We have established that the copolymerization of TA and NB can be readily achieved utilizing the system TiCl₃ + AlCl₃. A one-pot procedure was followed in which monomers, TiCl₃ and AlCl₃ were mixed in chlorobenzene at room temperature. Then the reaction vessel was put in a pre-heated oil bath (at ca. 130°C). The resulting product was a yellow to brown powder of good yield. Doping with iodine led to an enhancement of its electrical conductivity (from 10⁻¹⁴ to 10⁻⁹ S/cm). The product itself is paramagnetic (10¹⁷ sp/g, $g \sim 2.00$). It has a broad monomodal molecular weight distribution. Its IR spectrum has absorbency peaks corresponding to aromatic, olefinic and aliphatic C–H vibrations as well as peaks for C–O vibra-

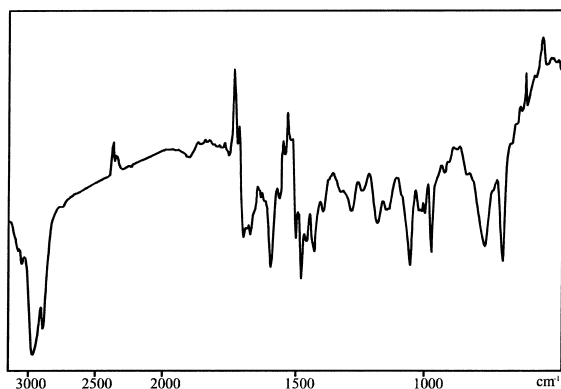


Fig. 1. IR spectrum of the oligomer product.

tions (Fig. 1). The weak ^1H NMR resonances at 10 ppm can be assigned to aldehyde end groups (Fig. 2). UV/VIS absorption occurs in the range of 250–450 nm with a maximum at 260 nm (Fig. 3). The maximum typical of PPV does not appear in the spectrum. However, its luminescence spectra are similar to those of PPV [13,14] (Fig. 3). All these facts show that: (i) the oligomers are single species whose molecule is composed of aromatic (originating from TA) and non-aromatic (originating from NB) structures; (ii) the degree of polymerization for the conjugated blocks varies ($n \geq 1$) but mostly $n = 1$. It is evident that conjugated blocks of TA are present, but the ring-opened structures originating from NB are not. However, the intensity of aliphatic and non-aliphatic resonances in ^1H NMR spectra estimates ca. 1:1 molar ratio of

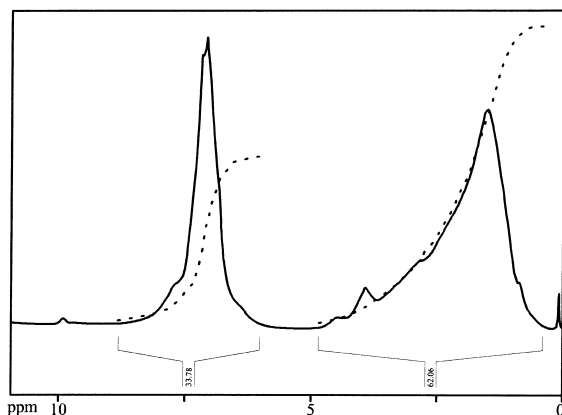


Fig. 2. ^1H NMR spectrum of the oligomer product.

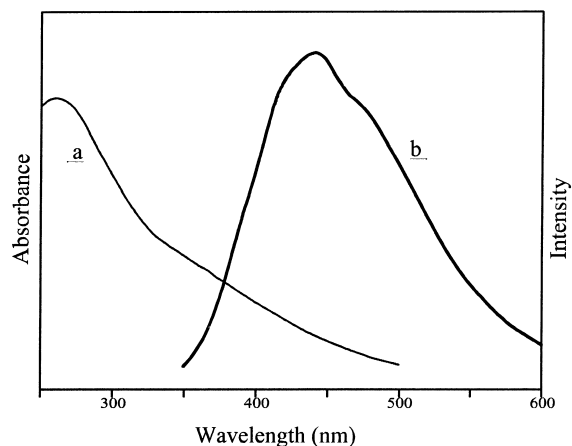


Fig. 3. (a) Absorption (left-hand-side ordinate) and (b) emission (right-hand-side ordinate, $\lambda_{\text{ex}} = 350$ nm) spectra of the oligomer product.

the units originating from TA and NB. NB blocks must also be present. The lack of resonances at 5.25 and 5.45 ppm shows that there are no *cis*- or *trans*- non-conjugated double bonds [15]. The NB units must therefore be incorporated by addition across the double bond, not by ring-opening.

It is known that with certain catalysts, NB polymerization by addition across the double bond is favoured at higher temperature [16]. Our experiments were performed at 130°C which may explain why non-conjugated double bonds are missing. The experiments run at lower temperatures with the assumption that NB will be able to incorporate by methathesis ring-opening resulted in low or none yield of the copolymer.

4. Conclusion

We succeeded for the first time in copolymerizing a conjugated dicarbonyl compound with a strained cycloolefin. The structure of the product is in accordance with the hypothesis that RC and COER run simultaneously under the influence of the binary system: transition metal halide + Lewis acid. For the time being, the way NB incorporates into the main chain is still not elucidated. Although the mechanism of

this transformation is much more complicated than we had expected, the synthesis itself is a very simple one-pot procedure. The investigations on the subject are at their beginning. Further studies should be done in order to interpret more precisely the structure of the products, to increase the molecular weight, to improve the molecular weight distribution, to tune the length of the conjugated blocks, etc. However, this work is a new route to soluble and processable copolymers containing conjugated blocks with valuable properties like electrical conductivity, non-linear optical response, electro- and photoluminescence, etc.

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