

# The synthesis, characterization and electro-optical properties of poly(pentenylene-*b*-acetylene)

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(Received 29 September 1988; revised 10 January 1989; accepted 19 January 1989)

Block copolymers containing polyacetylene and polypentenylene segments were synthesized by sequential addition of cyclopentene and acetylene to an active metathesis catalyst system. The ring-opening polymerization of cyclopentene was performed using  $WCl_6/AlEtCl_2$  as catalyst. The polypentenylene chains produced were terminated by tungsten complexes, which formed the loci of acetylene monomer polymerization. By controlling the block length of the 'solubilizing' block, a range of materials that had differing solubilities was produced. The polypentenylene block length could be shortened by incorporating a linear alkene in the cyclopentene ring-opening polymerization step. Preliminary electro-optical measurements support the view that soluble polyacetylene copolymers exist as a polydisperse distribution of optically anisotropic aggregates.

(Keywords: polyacetylene; block copolymer; electro-optical properties; metathesis; ring-opening polymerization)

## INTRODUCTION

Recently, significant interest has been aroused by the observation that certain polymeric materials may exhibit electrical and electro-optical properties which are quite unlike those shown by the vast majority of organic compounds. For example, the polyconjugated polymer polyacetylene may be doped with reagents such as iodine to produce a material that possesses an electrical conductivity which may be as high as that of typical metals like copper.

Polyacetylene may be synthesized directly from acetylene using coordination catalysts of the Ziegler-Natta<sup>1</sup>, Luttinger<sup>2</sup> or metathesis<sup>3</sup> type. The product is commonly an intractable, morphologically heterogeneous powder or film that is insoluble in common solvents and unstable towards oxidative degradation by air and moisture. These characteristics make the material difficult to process and result in poor in-service performance, thus limiting the potential applications for this polymer.

Several derivatives of polyacetylene have been synthesized, some of which are soluble in common solvents. Unfortunately, in most cases, derivatization severely disrupts the conjugated structure of the polyene chain, yielding materials in which the interesting electrical properties of polyacetylene are absent or dramatically reduced.

Soluble block copolymers containing polyacetylene segments have been prepared by various routes<sup>4</sup>. In these materials, the polyene backbone remains intact, enabling its properties to be examined in solution.

The work presented in this paper utilizes a copolymerization reaction (*Figure 1*) that involves sequential addition of the comonomers, cyclopentene and acetylene, to an active metathesis catalyst system. The salient synthetic details have been published elsewhere<sup>5</sup>. Here we show how the synthetic conditions may be manipulated to effect control over the respective block lengths of the two constituent polymer chains and present some preliminary results concerning the electro-optical properties of the copolymer in solution.

## CHARACTERISTICS OF POLY(PENTENYLENE-*b*-ACETYLENE)

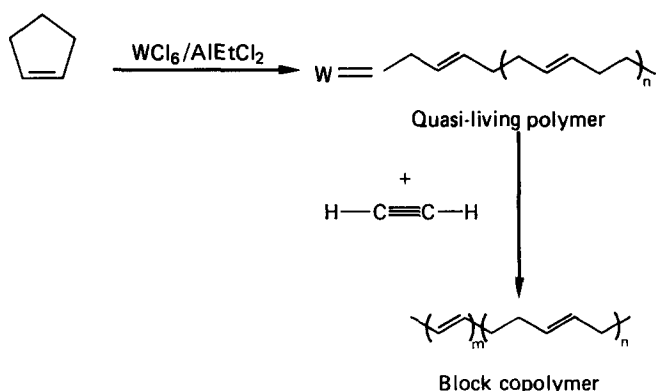
Poly(pentenylene-*b*-acetylene) prepared by the route outlined in *Figure 1* is a black elastomeric material, which can be dissolved in a range of common organic solvents to produce highly coloured solutions even at low concentration.

The u.v./vis. spectrum of a solution of the copolymer in cyclohexane is shown in *Figure 2*. In addition to the peak at 214 nm, which is characteristic of the polypentenylene backbone double bonds, a broad absorption, centred at 400 nm, extends well into the visible region. This peak is characteristic of the polyene chains in solution. When this spectrum is compared with a series of polyene,  $Me-(CH=CH)_n-Me$ , spectra, it can be concluded that the copolymer material contains a distribution of polyene chain lengths that are relatively short, the average length being estimated as  $n = 10$ .

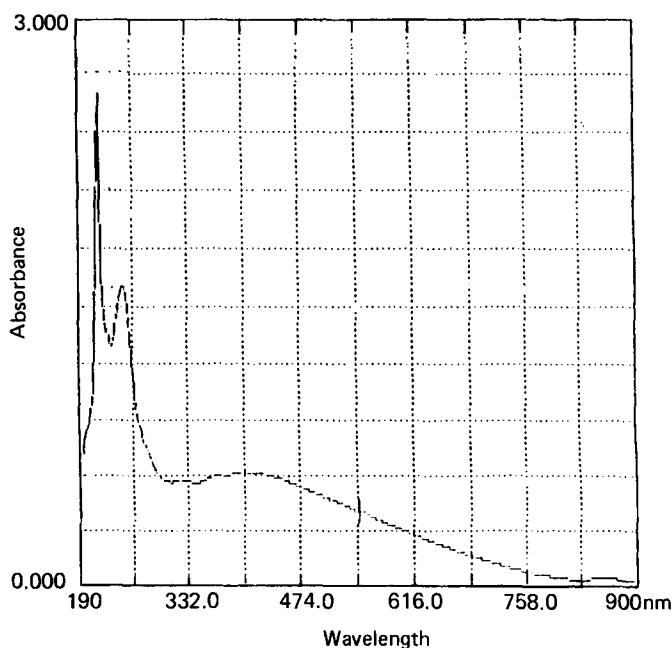
Gel permeation chromatographic (g.p.c.) data for a 1% solution of the copolymer in tetrahydrofuran (THF) is shown in *Figure 3*. The column eluent was analysed by two detectors connected in series, a differential

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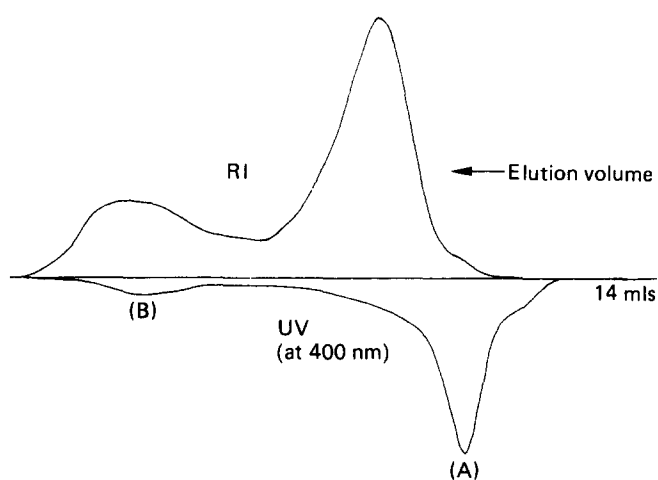
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**Figure 1** Synthesis of poly(pentylene-*b*-acetylene) by sequential addition of the monomers to an active metathesis catalyst



**Figure 2** U.v./vis. absorption spectrum of a 1% w/v solution of poly(pentylene-*b*-acetylene) in cyclohexane

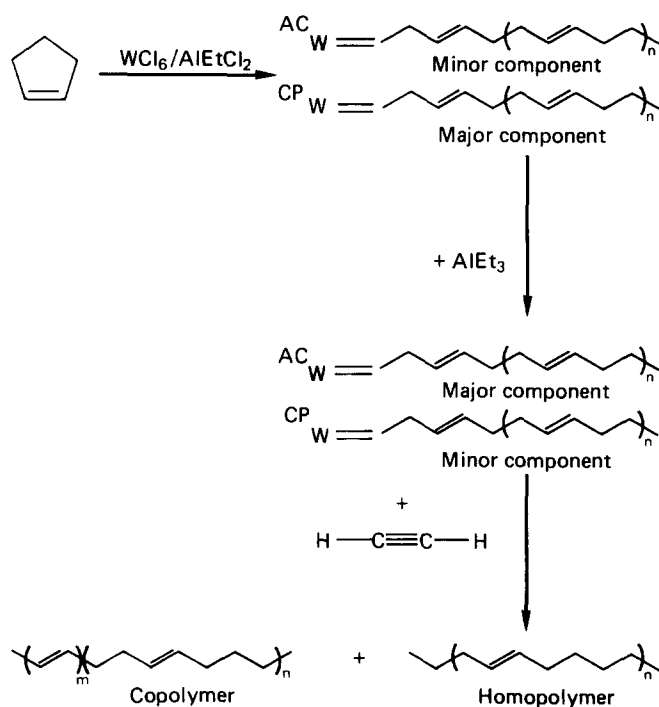


**Figure 3** Gel permeation chromatogram for a 1% solution of poly(pentylene-*b*-acetylene) in tetrahydrofuran

refractometer and a variable-wavelength u.v./vis. absorption spectrometer. Apart from the bimodal distribution, which is characteristic of polypentylene prepared by ring-opening metathesis polymerization, the refractometer trace also exhibits a small shoulder at high molecular weight ( $> 10^6$  relative to polystyrene). This small peak may be correlated with a strong u.v./vis. detector response, indicating that it originates from the same material that gives rise to the broad polyene absorption observed in the u.v./vis. spectrum of the copolymer. If this peak is due to copolymer, then it must be concluded that the samples contain only modest amounts of copolymer in an excess of unreacted homopolypentylene. The observed increase in molecular weight upon copolymerization cannot be explained in terms of the addition of a short ( $\sim 10$  acetylene units) polyene segment to polypentylene chains of  $\bar{M}_n = 2 \times 10^5$ . This conclusion suggests that the polyene chains of the copolymer aggregate to form large micellar-type structures.

#### ACTIVE SITE TRANSFORMATION REACTION

Although the route outlined in *Figure 1* has been shown to produce copolymer, the product is a mixture of homopolypentylene and copolymer, which is difficult to separate. The yield of copolymer can be increased by employing a route that involves a transformation reaction as shown in *Figure 4*. This scheme is based on the observation that  $\text{WCl}_6/\text{AlEtCl}_2$  is a poor catalyst for the polymerization of acetylene<sup>3</sup> but will give good yields of high-molecular-weight polypentylene. Conversely, the  $\text{WCl}_6/\text{AlEt}_3$  catalyst will efficiently polymerize acetylene but yields only modest amounts of high-molecular-weight polypentylene. It may be concluded that the catalytic species that polymerizes cyclopentene is not identical to the one responsible for acetylene polymerization. If cyclopentene is first polymerized using



**Figure 4** Synthesis of poly(pentylene-*b*-acetylene) using an active site transformation reaction

WCl<sub>6</sub>/AlEtCl<sub>2</sub> and then AlEt<sub>3</sub> is added, the number of catalytic sites that are active towards acetylene increases, which results in a greater proportion of copolymer relative to homopolymer in the product of the copolymerization reaction.

### CONTROL OF BLOCK LENGTH

The transformation scheme allows some control over both the acetylene and polypentenylene blocks. This may be demonstrated by considering the effect of varying the [AlEt<sub>3</sub>]/[AlEtCl<sub>2</sub>] ratio used in the copolymerization on the u.v./vis. spectrum of the copolymer produced. The results quoted in Table 1 show that, as the [AlEt<sub>3</sub>]/[AlEtCl<sub>2</sub>] ratio increases, the maximum of the broad polyene absorption moves to progressively longer wavelengths, indicating an increase in the average conjugation length, which is presumably due to an increase in the average length of the polyacetylene segments of the copolymer.

It is well known that the incorporation of a linear alkene during the ring-opening metathesis polymerization of a cyclic olefin results in a decrease in the molecular weight of the polymer formed. A series of copolymerizations of cyclopentene and acetylene were performed in which various concentrations of 1-octene were included. A sample of polypentenylene was taken from the reaction medium during a transformation copolymerization prior to the addition of acetylene and the relative molecular weight of the polymer estimated by g.p.c. The decrease in the molecular weight of polypentenylene as a function of the concentration of 1-octene is shown in Table 2. As the molecular weight of the polypentenylene decreases, the copolymer changes from a blue/black soluble elastomer to a black insoluble powder. It is noted that the time interval between the addition of acetylene to the active polymerizate and the detection of insoluble material decreases with decreasing polypentenylene molecular weight. This observation indicates that the shorter the polypentenylene chain, the less efficient it is in solubilizing the growing polyacetylene chain.

**Table 1** Effect of varying the [AlEt<sub>3</sub>]/[AlEtCl<sub>2</sub>] ratio on the u.v./vis. spectrum of the copolymer

Sample	$\lambda_{\max}$ (nm)	[AlEt <sub>3</sub> ]/[AlEtCl <sub>2</sub> ] <sup>a</sup>
1	452	0.4
2	550	1.0
3	593	3.0

<sup>a</sup> [WCl<sub>6</sub>]:[AlEtCl<sub>2</sub>] = 1:4

**Table 2** Effect of [1-octene] on  $\bar{M}_n$  of polypentenylene<sup>a</sup>

Sample	[CP]/[Octene]	$\bar{M}_n^b$	$t$ (min) <sup>c</sup>
1	0	$1.7 \times 10^5$	Soluble
2	$1.5 \times 10^{-3}$	$5.5 \times 10^4$	960
3	$8.3 \times 10^{-3}$	$1.3 \times 10^4$	180
4	0.016	$1.2 \times 10^4$	4
5	0.5	$1.0 \times 10^3$	1

<sup>a</sup> [WCl<sub>6</sub>] =  $2.3 \times 10^{-3}$  M; [Cyclopentene] = 3 M; [WCl<sub>6</sub>]:[AlEtCl<sub>2</sub>]:[AlEt<sub>3</sub>] = 1:4:4

<sup>b</sup>  $\bar{M}_n$  is the number-average molecular weight of polypentenamer relative to standard samples of polystyrene

<sup>c</sup>  $t$  is time interval (minutes) between addition of acetylene to the active polymerizate and the detection of insoluble material

### ELECTRO-OPTICAL PROPERTIES

The electro-optical properties of 1% w/v solutions of poly(pentenylene-*b*-acetylene) were examined using electrically induced birefringence and linear electric dichroism measurements.

If two orthogonal axes are chosen, one of which passes through the major molecular axis of an optically anisotropic molecule, then the refractive indices for light propagating along each of the two axes will be different. If these molecules are packed into a crystal lattice, then generally there will be a macroscopic difference in the refractive index for light propagating parallel ( $n_{\parallel}$ ) and perpendicular ( $n_{\perp}$ ) to the main crystal axis. This difference in refractive index,  $\Delta n = n_{\parallel} - n_{\perp}$ , is called the birefringence.

Birefringence can also be induced in a solution of optically anisotropic molecules by applying an electric field. Permanent and induced dipoles couple with the field and cause a reorientation which tends to result in a small net alignment of the molecules with respect to the direction of the applied electric field.

The electrically induced birefringence of solutions of the copolymer was measured using a relatively simple optical arrangement consisting of a helium-neon laser ( $\lambda = 632.8$  nm), a Glan-type polarizer oriented such that the plane of polarization of the emergent light was at 45° with respect to the electric field and a Glan-type analyser (positioned after the Kerr cell) crossed relative to the polarizer. Therefore, in the absence of an electric field, no light was transmitted. When a pulsed electric field was applied, the beam of light transmitted from the Kerr cell was generally elliptically polarized. A quarter-wave retarding plate placed directly after the cell converted the light into plane-polarized form such that the new plane of polarization was displaced by an angle  $\alpha$  from its original (zero-electric-field) direction. The electrically induced phase retardation ( $\delta$ ) between the two components of light travelling parallel and perpendicular to the direction of the applied electric field is:

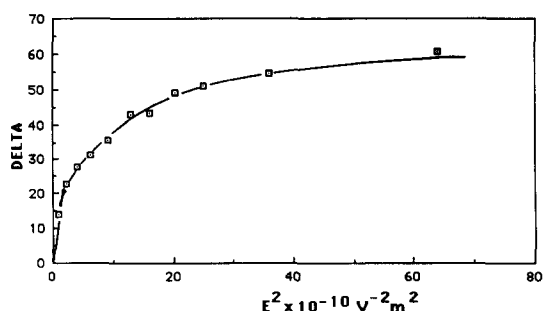
$$\delta = 2\pi\Delta n l / \lambda = 2\alpha$$

where  $l$  is the optical path length of the Kerr cell.

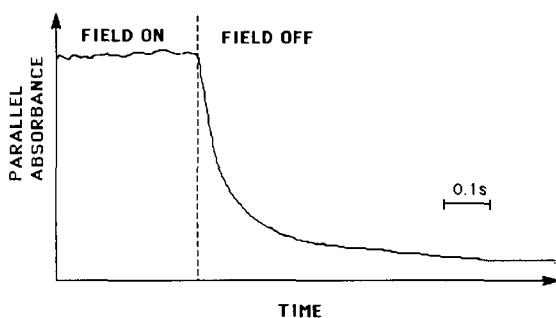
For a solution of molecules that absorb light, the application of an electric field induces dichroic effects in addition to birefringence, manifested by a difference in the absorbance of light parallel ( $A_{\parallel}$ ) and perpendicular ( $A_{\perp}$ ) to the electric field. The electrically induced dichroism,  $\Delta A = A_{\parallel} - A_{\perp}$ , is readily measured using a single-polarizer technique<sup>6</sup>. If the applied field is in the form of a rectangular voltage pulse, then a transient optical signal results. The transient dichroism exhibited by solutions of the copolymer was measured for light propagating with the plane of polarization parallel to the direction of the applied electric field, the signal being detected by a photomultiplier, electrically recorded and displayed on an oscilloscope.

The equilibrium value of the electrically induced birefringence provides information concerning the magnitude and type of the dipoles (permanent or induced) of the solute molecule present in solution. The decay of birefringence or dichroism following the removal of the applied field can provide information concerning the size, size distribution and shape of the particles in solution.

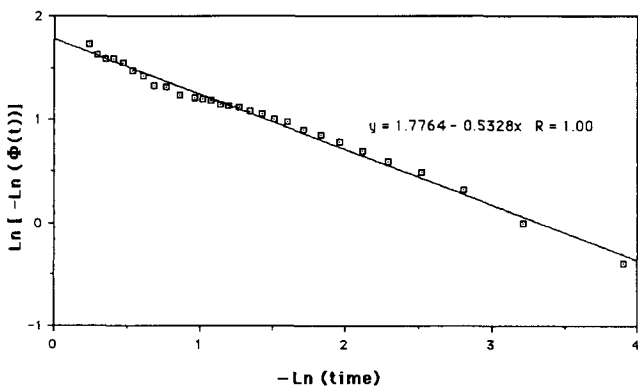
Figure 5 shows the dependence of  $\delta$  on the square of the applied field strength,  $E^2$ , for a 1% solution of



**Figure 5** Dependence of the induced phase retardation ( $\delta$ ) in degrees on the square of the applied field strength ( $E^2$ ) for a 1% solution of poly(pentenylene-*b*-acetylene) in cyclohexane at 298 K



**Figure 6** Transient decay curve of linear electric dichroism obtained using a 1% w/v solution of poly(pentenylene-*b*-acetylene) in cyclohexane at 298 K



**Figure 7** Analysis of the transient decay of electric dichroism using the Williams-Watts empirical relationship

copolymer in cyclohexane at 298 K. For small organic molecules, such plots are usually linear and obey the so-called Kerr law ( $\Delta n = BE^2\lambda$ )<sup>7</sup>. For large particles that couple strongly with the applied field, like those expected to be present in the aggregated copolymer, saturation effects become significant, causing the observed deviation from linearity. At very low field strengths, graphs of  $\delta$  vs.  $E^2$  do become linear, and by comparison of the initial slope of the curve with the slope obtained for the standard, toluene, the experimental Kerr constant  $B_{12}$  of the copolymer solution is estimated to be  $2.61 \times 10^{-11} \text{ V}^{-2} \text{ m}$ .

The transient decay of the parallel absorbance ( $A_{\parallel}$ ) is shown in *Figure 6* and cannot be described by a simple exponential function using a single relaxation time. Because of the non-exponential nature of the decay transients, they were analysed by the empirical relation of Williams and Watts<sup>8</sup>:

$$\phi(t) = \exp[-(t/\bar{\tau})^\beta]$$

where  $\phi(t)$  is the transient value of the induced birefringence or dichroism at time  $t$ ,  $\bar{\tau}$  is the mean relaxation time, a constant for a given system, and  $\beta$  is a constant indicative of the degree of polydispersity. A double logarithmic plot of  $\phi(t)$  vs.  $t$  as shown in *Figure 7* allows the constants  $\bar{\tau}$  and  $\beta$  to be estimated. For the optical transient shown in *Figure 6*,  $\bar{\tau}$  was found to be 35 ms. This value is considerably slower than the rotational relaxation time that results from the segmental motion of typical polymer chains ( $\sim 10^{-8}$  to  $10^{-10}$  s). The empirical parameter  $\beta$  was found to be close to 0.5, indicative of a polydisperse distribution of particle sizes and/or a broad distribution of relaxation processes. Preliminary data obtained using photon correlation spectroscopy (Dr Rarity, RSRE, Malvern) suggest that the copolymer particles possess effective hydrodynamic diameters in the range 0.1–1  $\mu\text{m}$ , however this analysis assumes that the particles are spherical.

The preliminary electro-optical data described in this paper support the view that poly(pentenylene-*b*-acetylene) exists as a polydisperse distribution of optically anisotropic aggregates in solution. Work concerned with determining the shape and structure of the aggregates is currently in progress.

## ACKNOWLEDGEMENT

T. R. Farren and J. A. Stowell wish to thank Aston University for the provision of financial support during the course of this project.

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