Polymer Bulletin 29, 527–533 (1992)

Polymer Bulletin

In situ infrared kinetic study of the thermal conversion of polyphenylene-1,2-dibromoethylene to polyphenyleneacetylene

V. L. Patel, S. P. Church*, and N. Khan

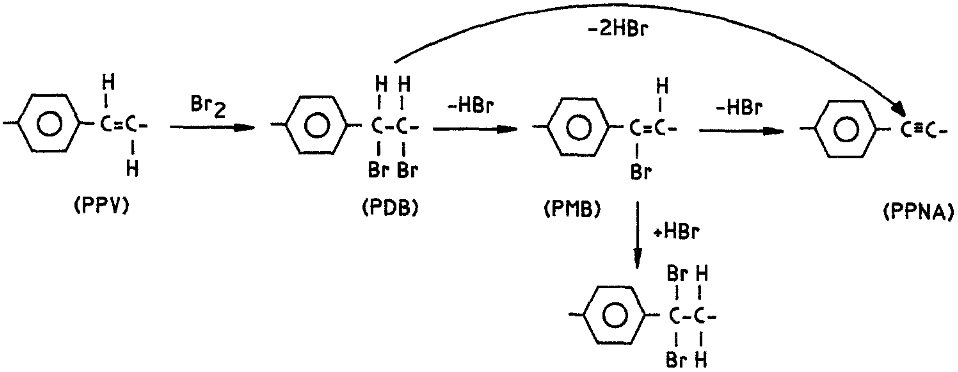
Courtaulds Research, P.O. Box 111, Lockhurst Lane, Coventry, CV6 5RS, UK

Summary

The thermal reaction of polyphenylene-1,2-dibromoethylene under argon flow has been investigated using *in situ* kinetic infrared spectrocopy. Between 200 and 250°C, the reaction proceeded via elimination of HBr with first-order rate constants in the range of 1.98×10^{-5} - 3.08×10^{-4} s^{-1}. The product formed was a copolymer containing phenyleneacetylene linkages partially interrupted by brominated units. The activation energy of 113 KJ mol^{-1} was considerably below the C-Br bond dissociation energy.

Introduction

The synthesis of conducting polymers via precursor routes has been the subject of much attention in recent years. This approach has been demonstrated for the production of fully conjugated polymers such as polyacetylene (1), polyphenylene (2) and polyphenylenevinylene (PPV) (3). Hsieh (4) has recently extended the PPV system to encompass additional steps leading to the formation of polyphenyleneacetylene (PPNA) (Scheme 1)



Scheme 1

---

*Corresponding author

One particularly interesting reaction is the dehydrobromination of polyphenylene-1,2-dibromoethylene (PDB) to PPNA (Scheme 1). Since this reaction involves the loss of two HBr molecules per repeat unit, a stepwise elimination of HBr via a polyphenylenemonobromovinylene (PMB) intermediate may be envisaged. Alternatively, PPNA may form directly through loss of 2 HBr molecules where no intermediate is observed. The further possibility of back reaction of HBr with PMB to form polyphenylene-1,1-dibromoethylene may also be involved. Indeed, it is worth noting that Hsieh's PPNA (4) was not obtained as the pure homopolymer suggested by Scheme 1, but rather as a copolymer containing phenyleneacetylene blocks interrupted by bromine containing units.

Infrared spectroscopy is ideally suited to the study of thin polymer films. If the polymer is undergoing some kind of temporal change, then this can be conveniently monitored _in situ_ in the infrared spectrometer. Such an approach has been adopted by Foot _et al_ (5) in a kinetic study of the precursor route to polyacetylene. With the advent of FTIR spectrometers, full-range infrared spectra can be generated in very short time periods. The application of FTIR spectroscopy with its powerful fingerprinting capability to the study of chemical reactions is a desirable extension of the technique. In addition, software routines allow the adaptation of the "frequency-rich" FTIR spectra recorded at different time intervals to "time-rich" kinetic plots. This work describes how these principles can be applied to the kinetic analysis of the conversion of PDB to PPNA.

Experimental

PDB films were prepared by bromination of PPV films in chloroform solution according to the literature procedure (4). Complete conversion to PDB was confirmed by infrared spectroscopy and elemental analysis. PDB films (_ca_. 6 µm thick) were mounted in a SPECAC variable temperature infrared cell equipped with potassium bromide shroud window to enclose the film. Before any heating, the cell was first conditioned with a slow, but steady stream of argon (25 ml min^{-1}) for 1 hour. Whilst maintaining the argon flow, the cell was then heated to the appropriate temperature (200, 212, 225, 237, 250°C) corresponding to five separate isothermal runs. The temperature was allowed to equilibrate for 10-15 minutes before each run was started. Infrared spectra were then recorded on a Nicolet 510 FTIR spectrometer using a computer macro routine. The basis of the collection was to store sequential spectra in sequential files corresponding to 10 minute time periods. This time period was found to be sufficiently short in terms of the overall timescale of the reaction. Spectra corresponding to each time interval (or data point) were stored on disc and were further analysed in terms of peak area (integrated absorbance) versus data point (time) using further computer macro routines. In this way, the "frequency-rich" FTIR spectra could be converted into "time-rich" kinetic plots. These plots were then evaluated in terms of exponential fits using standard curve fitting routines.

Results and Discussion

Figure 1 shows an overlay of spectra recorded at successive 1 hour intervals for the reaction of PDB at 225°C. This diagnostic region of the spectrum clearly illustrates the disappearance of the intense C-Br stretching vibration of PDB at 617 cm^{-1} and the appearance of a weaker band at 590 cm^{-1} with time. Note the isobestic point at 597 cm^{-1} which is in accord with a simple first-order A to B conversion. "Time-rich" kinetic plots illustrating the integrated absorbance changes within specific frequency ranges are displayed in Figure 2. For convenience the ordinate (integrated absorbance) scales of the 6 plots have been normalised. Figure 2a and 2b correspond to C-Br stretching and aliphatic C-H stretching bands of PDB, respectively. These absorptions are clearly disappearing on the same timescale and indicate reaction of the 1,2-dibromoethylene moieties via loss of H and Br. The four "grow-in" plots displayed in Figure 2c-2f illustrate the concurrent formation of product bands. The most significant of these plots is Figure 2f which shows the appearance of a band in the C≡C stretching region. The concurrent formation of all these bands (Figure 2c-2f) group these features to a common product.

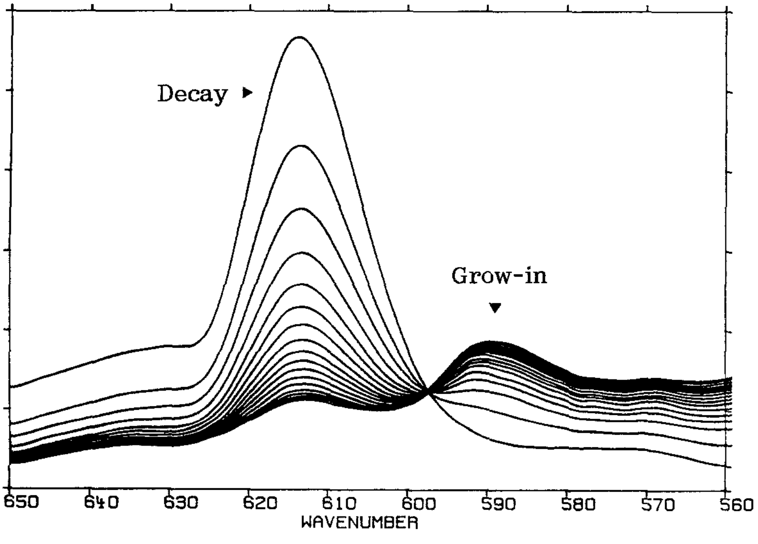


Figure 1. Overlay of infrared spectra recorded at successive one hour intervals for the reaction of PDB at 225°C

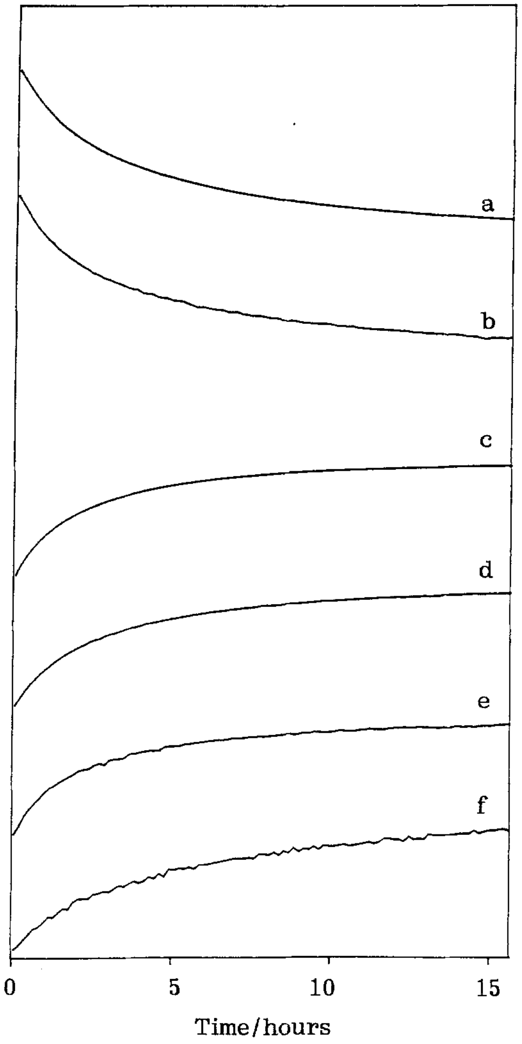


Figure 2. Normalised integrated absorbance versus time plots for the reaction of PDB at 225°C. (a) Decay of C-Br stretching in PDB (630-597); (b) Decay of aliphatic C-H stretching in PDB (3000-2900); (c) Formation of ≡C-Ar stretching in PPNA (976-935); (d) Formation of =C-Br stretch in PPNA (597-577); (e) Formation of ring deformation mode in PPNA (562-528); (f) Formation of C≡C stretching mode in PPNA (2230-2170). The numbers in parentheses refer to the wavenumber range used for the integrated absorbance measurements.

These features may be traced to the formation of PPNA which can be described as a copolymer consisting of phenyleneacetylene linkages partially interrupted by brominated units (4). It is interesting to consider the formation of the band at 590 cm^{-1}, tentatively assigned by Hsieh (4) to =C-Br stretching in the PPNA copolymer, in more detail. From Figure 1 and Figure 2d, it can be seen that this band grows in concurrently with the decay of PDB. If we monitor the time-dependence of this band at 250°C (Figure 3a), we notice the anticipated exponential increase in absorbance followed by a second slow decay process. This is in accord with Hsieh's assignment and suggests that the PPNA copolymer reacts further by a much slower process involving consumption of monobromovinylene units. It is perhaps surprising that the decay of PDB leads to the formation, at least in the initial reaction, of a copolymer of relatively uniform composition. Bromine determinations suggest that the PPNA copolymer contains 1 bromine atom per 3 phenyleneacetylene units. This would be in keeping with a 3:1 phenyleneacetylene/ phenylenemonobromovinylene copolymer. It is interesting to note the time-dependence of the absorbance changes in the aliphatic C-H stretching region at 250°C (Figure 3b). The initial decrease in absorbance corresponds to the consumption of 1,2-dibromoethylene units, cf. Figure 2b. The slower second process which leads to an increased absorbance in this region is presumably associated with the formation of 1,1-dibromoethylene units which would be anticipated to absorb here. This finding concurs with the behaviour of the 590 cm^{-1} band described above and strongly suggests that the second process involves, at least in part, back reaction of monobromovinylene with HBr (see Scheme 1). Clearly the overall reaction processes may be very complex and factors such as diffusion of HBr and film thickness are likely to be significant. For instance, it may be envisaged that there is an excess of acetylene linkages at the surface where HBr can be efficiently removed from the system.

Temperature Measurements

The first-order nature of the first-stage reaction of PDB to the PPNA copolymer was confirmed by the very good exponential fits which were obtained at all temperatures studied. The rate constants and half-lives are assembled in Table 1. It can be seen that the reaction is approximately 16x faster at 250°C compared with 200°C and that the half-life of reaction is less than 1 hour at 250°C.

TABLE 1. Rate constants and half-lives for reaction of PDB to PPNA

T (°C)	$10^5 k$ (s^{-1})	$t_{1/2}$ (hrs)
200	1.98	9.72
212	3.63	5.30
225	7.75	2.48
237	14.35	1.34
250	30.80	0.63

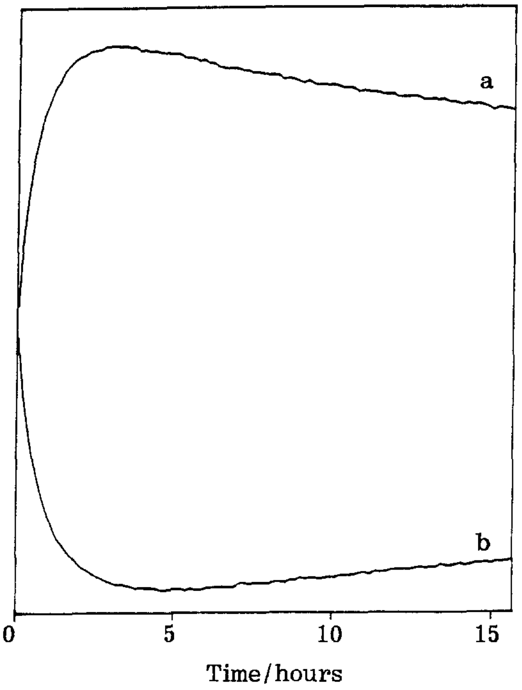


Figure 3. Normalised integrated absorbance versus time plots for the reaction of PDB at 250°C. (a) =C-Br stretch (cf. Figure 2d); (b) aliphatic C-H stretching region (cf. Figure 2b).

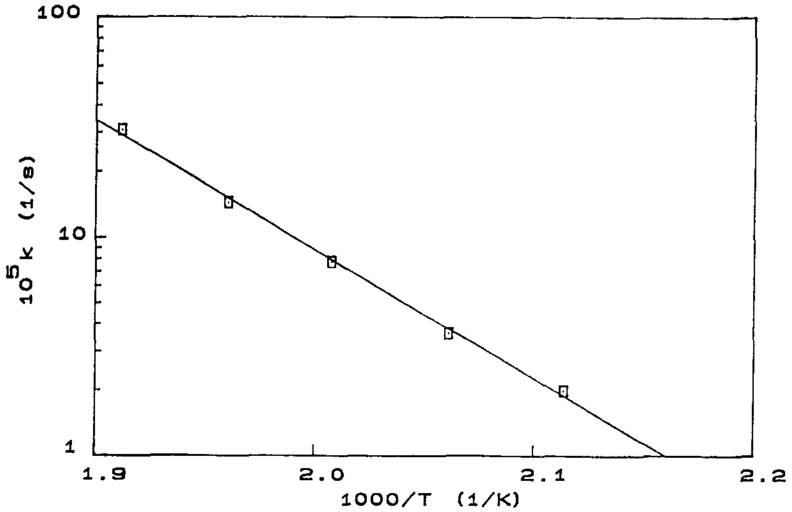


Figure 4. Arrhenius plot for the reaction of PDB

The data in Table 1 is presented as the Arrhenius plot in Figure 4, allowing the activation energy of 113 KJ mol^{-1} and the pre-exponential factor of 5.38×10^7 to be calculated. Interestingly, the activation energy is 2-3 times lower than the C-Br bond dissociation energy. This shows that the transition state involves only weakening of bonds and not bond cleavage.

Conclusion

In the range 473-523 K under argon flow, PDB undergoes thermal elimination of HBr to form PPNA with a first-order rate constant given by

$$k = 5.38 \times 10^7 \exp(-13600/T)\ s^{-1}$$

The PPNA copolymer which contains brominated units is relatively stable on the timescale of reaction investigated here but can react further by a much slower process. The *in situ* monitoring of a reaction by FTIR spectrocopy allows both structural and kinetic information to be obtained in the same experiment and has obvious advantages over more traditional techniques such as differential scanning calorimetry and thermogravimetric analysis where chemical information may only be deduced indirectly.

References

1. Edwards JH, Feast WJ, Bott DC (1984) Polymer 25: 395

2. Ballard DG, Courtis A, Shirley IM, Taylor SC (1983) J. Chem. Soc. Chem. Commun. 954

3. Bradley DDC (1987) J. Phys. D.: Appl. Phys. 20: 1389

4. Hsieh BR (1991) Polym. Bull. 25: 177

5. Foot PJS, Calvert PD, Billingham NC, Brown CS, Walker NS, James DI (1986) Polymer 27: 448

Accepted July 15, 1992 C