This article was downloaded by:
On: *24 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Thermal Characterization of Polybutadiyne

Arthur W. Snow[a]
[a] Naval Research Laboratory, Washington, D.C.

To cite this Article Snow, Arthur W.(1985) 'Thermal Characterization of Polybutadiyne', Journal of Macromolecular Science, Part A, 22: 10, 1429 — 1441

To link to this Article: DOI: 10.1080/00222338508063345

URL: http://dx.doi.org/10.1080/00222338508063345

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J. MACROMOL. SCI.–CHEM., A22(10), pp. 1429-1441 (1985)

Thermal Characterization of Polybutadiyne*

ARTHUR W. SNOW

Naval Research Laboratory
Washington, D.C. 20375

ABSTRACT

Butadiyne was thermally polymerized from the vapor phase onto substrate polyethylene, poly(vinylidene fluoride), polytetrafluoroethylene, and fluorinated ethylene propylene films at 20°C. The reaction is characterized as an initial absorption of monomer into the film followed by polymerization in the condensed state. A postpolymerization thermal reaction of the polybutadiyne pendant ethynyl groups was conducted over a 120 to 470°C temperature range with a subsequent surface electrical resistivity decrease to 7×10^{11} ohm/square. The reaction of the pendant acetylenic groups was monitored by DSC and IR spectroscopy and found to be more complex than an intramolecular conversion of an acetylenic polyene to a polyacene structure.

INTRODUCTION

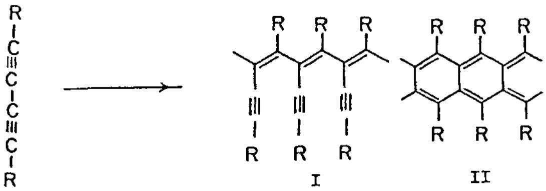
Butadiyne, C_4H_2, the simplest diacetylene, undergoes a facile thermal polymerization in the melt or from the vapor phase by selective deposition onto an organic substrate polymer film. This mode

---

*Presented at the IUPAC 28th Macromolecular Symposium, Amherst, Massachusetts, 1982.

0022-233X/85/2210-1429$3.50/0

of diacetylene polymerization is structurally distinct from the solid-state polymerization of diacetylenes which has been intensively investigated and characterized as yielding a polymer with a 1,4-repeat unit structure [1]. In the melt or solution, the polymerizations and polymer structures are less extensively characterized, with a combination of substituted polyene (I) and polyacene (II) structures having been proposed [2-4].



(1)

Examples where R is a phenyl [2], methyl [3], or pentafluorosulfur [4] substituent have been studied. The butadiyne polymer (R = H) presents a unique opportunity for characterizing the chain structure without interference from a pendant group.

Previous work from this laboratory [5] has demonstrated that polybutadiyne may be conveniently prepared and handled as a vapor-deposited film onto an organic substrate polymer such as polyethylene or Teflon. Bulk unsupported polybutadiyne is an insoluble, intractable substance. This polymer has been structurally characterized by IR, UV, and ESR spectroscopies as a polyconjugated chain with pendant, terminal acetylenic functional groups.

In the present study the postpolymerization thermal treatment of vapor-deposited polybutadiyne is investigated with the objective of developing a material possessing the viscoelastic properties of the substrate polymer film and an electrical conductivity comparable with that of current research polymers (i.e., 10^{-4} to 10^{-1} S/cm) [6]. The expectation of a significant electrical conductivity associated with the thermal treatment of the polybutadiyne is based on the hypothesis that the pendant acetylenic groups of structure I and would be converted to the ladder structure II. Such a structural speculation has accompanied a reported electrical conductivity increase of 12 orders of magnitude to a maximum of 10^{-2} S/cm when the poly(diphenylbutadiyne) system was subjected to a 700°C heat treatment [2a, 2b]. The attractive features of the simpler parent polybutadiyne system are: (1) the reaction of the terminal acetylenic group is easily monitored; (2) the higher reactivity on an unsubstituted acetylenic group suggests the reaction would occur at a lower temperature; (3) if the polybutadiyne could be converted to a moderately conducting material at reasonably low temperatures, a combination with its ease of application to substrate organic polymers could have important practical consequences; and (4) the polyacene structure is theoretically predicted to be capable of very high electrical conductivities [7]. The approach is to deposit polybutadiyne on a variety of substrate polymer films which include polyethylene (PE), poly(vinylidene fluoride) (PVF2), poly(tetrafluoroethylene) (PTFE), and poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP), and study the postpolymerization thermal reaction of polybutadiyne by DSC, TGA, IR, ESR, and electrical conductivity measurements.

EXPERIMENTAL

Butadiyne Synthesis

Butadiyne was prepared by the dehydrochlorination of 1,4-dichloro-2-butyne in aqueous potassium hydroxide-dioxane solution [8]. The crude product was vacuum distilled to IR purity [9]. This distillation is conducted from a -80°C trap to a -195°C trap at 10^{-4} torr to remove an impurity identified as 2-chloro-1-butene-3-yne [10]. This less volatile impurity is detectable in the infrared by strong bands at 850 and 1590 cm^{-1} where butadiyne is transparent. Other bands assigned to 2-chloro-1-butene-3-yne are observed at 620, 920, 1015, 1230, 1260, 1703, 2118, 3142, 3182, 3197, and 3328 cm^{-1}. By periodically monitoring infrared spectra (100 torr, 10 cm gas cell) of the distillate, we find 50 to 60% of the butadiyne has distilled before impurity bands begin to appear. The infrared spectrum of the purified butadiyne is identical to that of Ref. 9, and PMR (10% $CDCl_3$ solution) did not detect proton impurities. Care and precautions should be exercised in handing the butadiyne or detonation may occur on mixing with oxygen and warming [11].

Butadiyne Polymerization

Butadiyne thermopolymer samples were prepared by placing films of substrate organic polymers (low density polyethylene (PE) 3.7 mil, polyvinylidene fluoride (PVF2) 1.7 mil, polytetrafluoroethylene (PTFE) 2.8 mil, and poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP)) in an atmosphere of 700 torr butadiyne at 20°C for 5 weeks. The substrate films (4.0 × 1.5 cm) were previously cleaned by washing in 30% hydrofluoric acid for 1 min, rinsed with distilled water, and dried under vacuum in a 1-L Pyrex reactor before introduction of the butadiyne. The order of polymerization reactivity was PVF2 > PE > PTFE > FEP as determined by visual observation of a yellow-brown color development and the corresponding gravimetric weight percent increase (PVF2, 81%; PE, 61%; PTFE, 23%; FEP, 0.3%).

Postpolymerization heat treatment of the polybutadiyne-PTFE sample was conducted by sealing it in an evacuated Pyrex tube and placing the tube in a Lindberg tube furnace for 60-min periods at temperatures that ranged from 120 to 470°C in increment intervals of about 40°C. At the end of each period the tube was opened, the IR spectrum obtained, and the sample then returned to the tube which was reevacuated and sealed for thermal treatment at the next higher temperature. No flow or physical shape deformation of the sample was observed at temperatures above the PTFE melting point. A similar observation was made for the polybutadiyne-PE sample although in this case a control PE film melted and strongly adhered to the tube wall.

Characterization

DSC and TGA data were obtained from 10 mg samples in a nitrogen atmosphere at a 10°C/min heating rate using a Dupont 990 Thermal Analyzer, 910 Differential Scanning Calorimeter, and 951 Thermogravimetric Analyzer. X-ray diffraction data were obtained with a Phillips XRG-2600 (Ni filtered Cu$K\alpha$ radiation) x-ray diffraction unit. Postpolymerization heat treatments were conducted for 1 h periods at selected temperatures between 120 and 470°C in an evacuated, sealed Pyrex tube. Transmission IR spectra were recorded on a Perkin-Elmer 267 grating spectrophotometer. ESR spectra were recorded on a Bruker ER200D spectrometer. Surface resistivity measurements were made using an interdigital electrode array consisting of 50 "finger pairs" 25 μm in width and separated by 25 μm [12]. The upper measurement limit of this apparatus is 10^{13} ohm/square using a ± 2.5-V bias.

RESULTS

Polybutadiyne Preparation

From the vapor phase, butadiyne selectively polymerizes onto organic polymer films in preference to the Pyrex walls of its vessel [5]. Samples of polybutadiyne deposited onto PE, PVF2, PTFE, and FEP were prepared by thermal polymerization of butadiyne vapor onto thin films of these polymers at 20°C. To the eye the polybutadiyne appeared as a coating on the substrate film, ranging in color from brownish-yellow to shiny black depending on the quantity of polybutadiyne deposited. The coating conformed and flexed well with the substrate at low degrees of polybutadiyne deposition ($<$ 10% by weight of sample), although the sample gradually developed a stiff and brittle character as the polybutadiyne content approached a significantly large fraction (i.e., 50%).

The following observations and results are pertinent to describing the polymerization process and the characterization of the samples.

Examination of a cut cross-section of a PTFE sample showed a color concentration gradient ranging from a dark brown at the surface to a dark yellow at the center of the film. This indicates a significant penetration of the polybutadiyne beyond the surface of the substrate film.

The order of butadiyne polymerization selectivity for the substrate films as determined by gravimetric weight percent increase was PVF2 (81%) > PE (61%) > PTFE (23%) > FEP (0.3%).

X-ray diffraction patterns of the PTFE, PE, and PVF2 substrate films before and after polybutadiyne deposition are presented in Fig. 1. The crystallite diffraction maxima are reduced in intensity or disappear and the d-spacing has changed. No crystallite reflections have been observed from unsupported polybutadiyne bulk polymer samples [13].

The melting points of the substrate polymers were altered by the polybutadiyne deposition as measured by DSC (Fig. 2).

Samples prepared by this technique have properties that were particularly useful for subsequent experiments. In addition to a physical form for convenient handling, the dispersal of polybutadiyne was such that good quality infrared spectra may be obtained. The complementary infrared transmissions of the PE and PTFE films allowed for a complete spectrum of polybutadiyne to be represented (Fig. 4) which was much sharper than that obtained from a KBr pellet preparation of a bulk polybutadiyne sample. For DSC measurements the high thermal stability and relatively few thermal transitions of the PTFE substrate film left a significantly large temperature range available for observing the polybutadiyne thermal reaction.

DSC and TGA

To determine the temperature range that a postpolymerization thermal reaction may encompass, DSC thermograms of the substrate films before and after deposition of the polybutadiyne were obtained in a nitrogen atmosphere (Fig. 2). The blank films displayed their characteristic endothermic transitions and melting points: PE 110°C; PVF2 67, 163°C; PTFE 19, 30, 327°C; FEP 267°C. After deposition of the polybutadiyne, two significant changes were observed. First, a very broad exotherm ranging from 80 to approximately 400°C with a maxima between 200 and 250°C appeared in the thermogram of each sample. In the PTFE and FEP thermograms, a partially resolved secondary maxima at 110°C was also observed. The exotherm is associated with reaction of the pendant acetylenic groups. The second observation was significant changes in the substrate polymer transitions. In PTFE the melting point was elevated from 327 to 357°C while the 19 and 30°C transitions remained unchanged. The FEP melting point was slightly elevated from 267 to 273°C. In each case, two subsequent thermal cycles returned the melting point to the original value. The PVF2

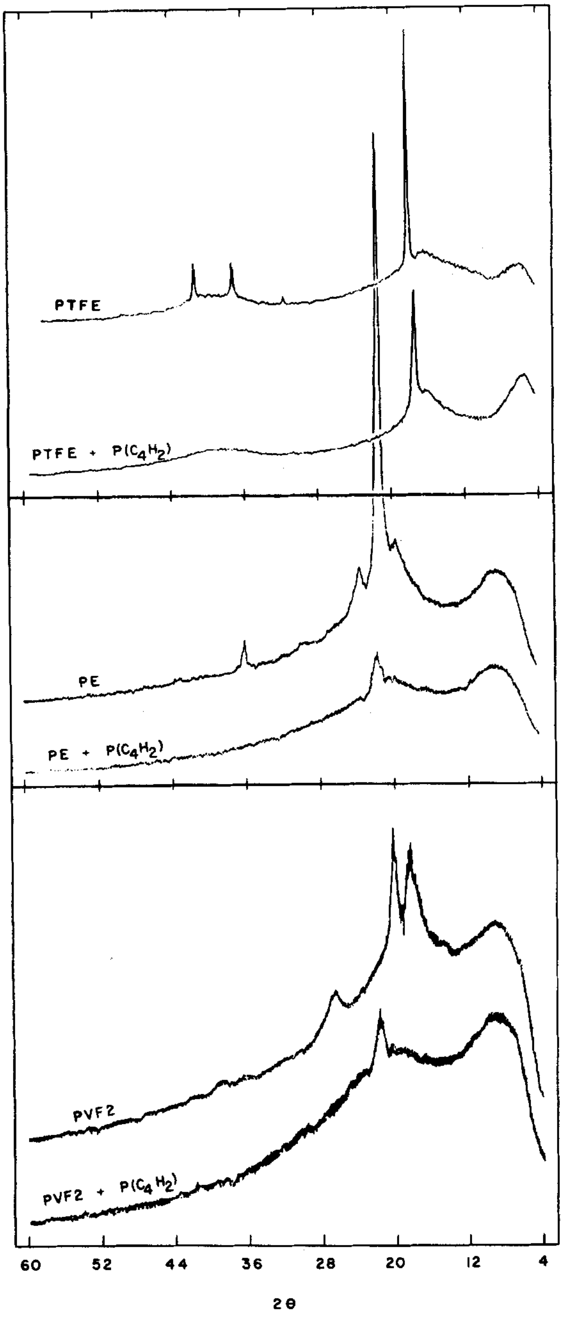


FIG. 1. Wide-angle x-ray scattering of the PTFE, PE, and PVF2 samples before and after polybutadiyne deposition.

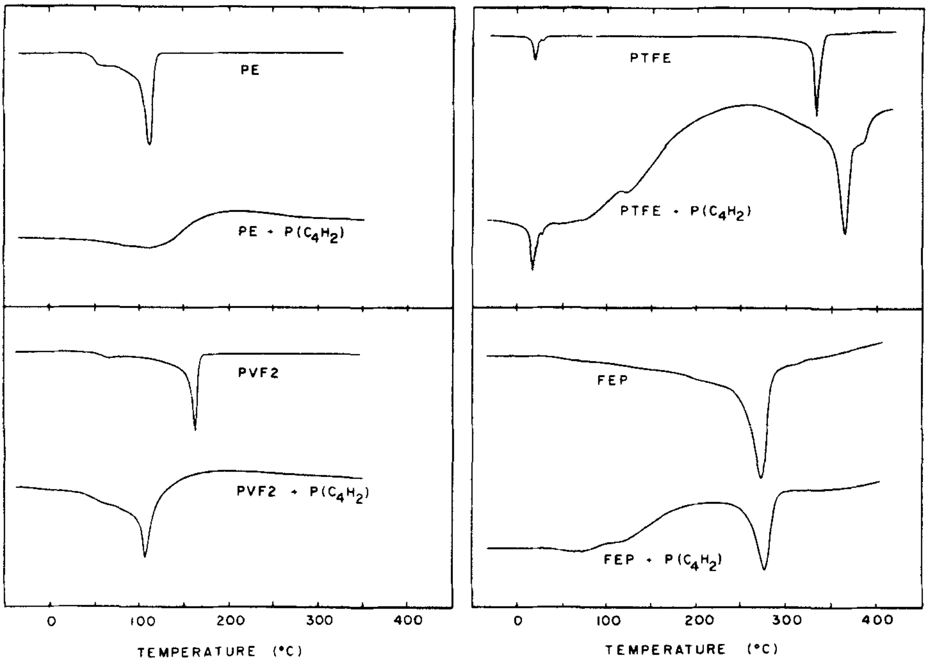


FIG. 2. DSC thermograms of PE, PVF2, PTFE, and FEP control and polybutadiyne deposited samples.

melting point was depressed from 163 to 113°C and did not recover on thermal cycling but approached a constant value at 105°C. The PE thermogram was radically changed, and the melting point was difficult to recognize. Thermal cycling did restore an endotherm maxima at 90 and 85°C on the second and third scans, respectively.

The TGA of the polybutadiyne-deposited samples and blank films were nearly identical except for a polybutadiyne residual weight. Thermograms of the PE and PTFE samples and blanks in a nitrogen atmosphere are presented in Fig. 3. For an unsupported bulk polybutadiyne sample, the weight loss is less than 6% [5c].

Spectroscopic Analysis

The polybutadiyne thermal reaction was monitored by IR spectroscopy as a function of heat treatment temperature. An IR spectrum of the initial polybutadiyne is presented in Fig. 4 without interference from the substrate film absorptions. The terminal acetylenic functional groups are indicated by the bands at 3315, 2090, and 640 cm^{-1}. The bands representative of a polyconjugated structure are

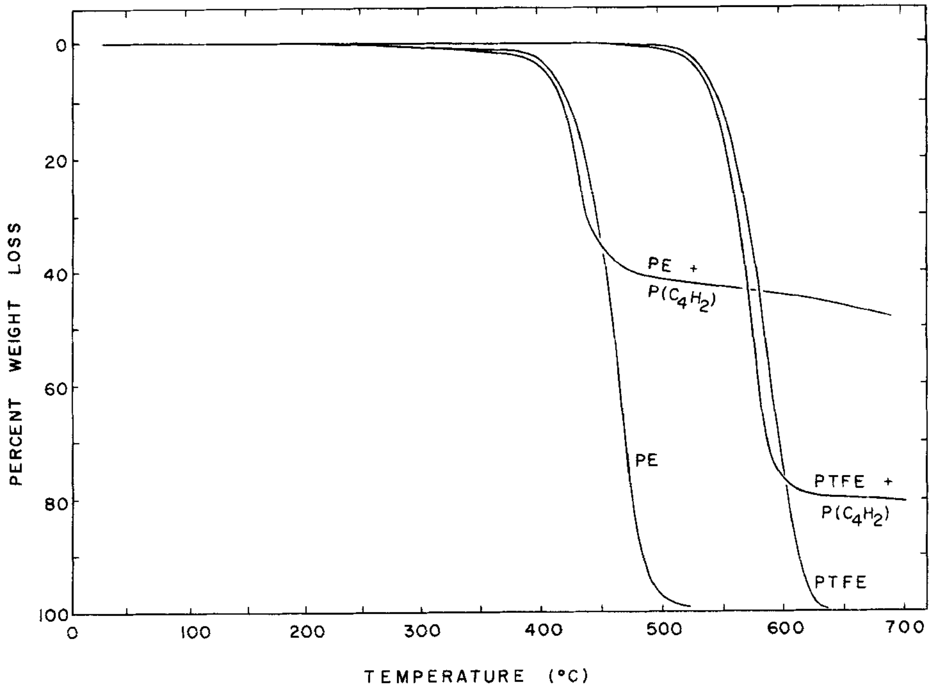


FIG. 3. TGA thermograms of PE and PTFE control and polybutadiyne deposited samples.

those at 1600, 1210, and 885 cm^{-1}. The 3020 cm^{-1} band is attributed to an aromatic carbon-hydrogen stretching while an apparent aliphatic carbon-hydrogen stretching band is not understood at present. A more detailed IR spectrum analysis of this polymer is presented in Ref. 5c.

The PTFE sample was used to monitor the polybutadiyne thermal reaction since it has a thermal stability ranging up to 500°C and a large infrared window. Heat treatments of the sample were conducted in an evacuated sealed Pyrex tube at temperatures ranging from 120 to 470°C in increment intervals of about 40°C. The acetylenic bands gradually diminished in intensity and were reduced by a factor of 10 at 310°C. The intensities of the 3315, 2090, 3020, 2935, and 1600 cm^{-1} bands, obtained as the difference between absorptions of the PTFE sample and a Teflon control film, are plotted against heat treatment temperature in Fig. 5. As the acetylenic absorptions decrease in intensity, the 3020, 2935, and 1600 cm^{-1} bands became more intense. The 885 cm^{-1} absorption was nearly unchanged. Heat treatments above the PTFE melting point resulted in a marked increase in the

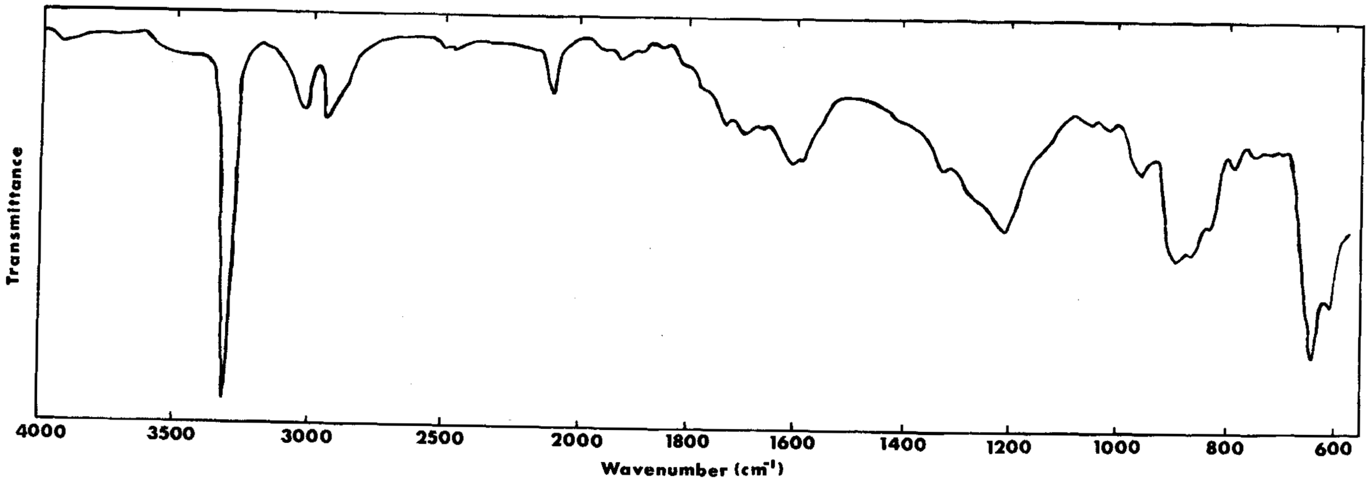


FIG. 4. IR spectrum of polybutadiyne obtained from PE and PTFE samples. PE and PTFE absorptions have been subtracted.

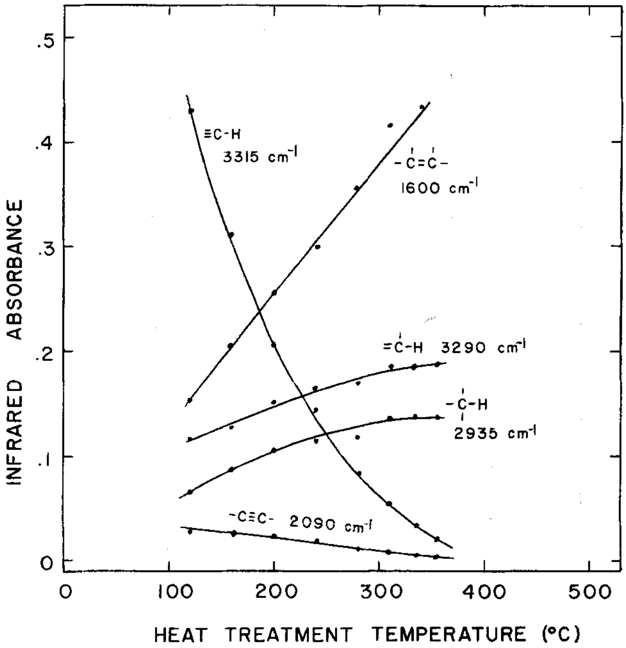


FIG. 5. Polybutadiyne infrared band intensity variation as a function of heat treatment temperature of a PTFE sample.

infrared scattering background and a much poorer resolution of the polybutadiyne bands. However, no gravimetrically detectable weight loss or physical shape deformation due to liquid flow of the PTFE substrate was observed.

The ESR spectrum of polybutadiyne has been characterized as an intense narrow Lorentzian shaped singlet at a free electron g-value [5b]. Thermal treatment of the PTFE sample up to 470°C resulted in a spin density increase from 8×10^{19} to 2×10^{20} spin/g and a Lorentzian linewidth narrowing from 12 to 1.5 G in vacuum. The signal was no longer insensitive to oxygen but displayed a pressure-dependent oxygen broadening where the linewidth increased from 1.5 to 6 G on admission of air.

Electrical Measurements

Surface resistivity measurements were made by mechanically pressing the polybutadiyne-PTFE sample against a surface interdigital electrode. The surface resistivity is obtained as the product of the measured resistance and the number of squares in the electrode array. (The size of the square is defined by the electrode separation distance. For the interdigital electrode of this experiment, there are 50 "finger pairs" with a 25-μm separation and a 7,250-μm overlap length giving (7,250 × 99)/25 = 28,700 squares.) The PTFE-polybutadiyne surface resistivity remained above the 10^{13} ohm/square measurement limit of the apparatus until the sample was subjected to heat treatment temperatures above 400°C. A surface resistivity of 7×10^{11} ohm/square was measured after a 12-h 470°C heat treatment.

DISCUSSION

The preceeding results indicate that both the butadiyne thermal polymerization and subsequent thermal reaction of the acetylenic pendant groups are more complex than depicted by the reaction and structures in Eq. (1).

The deposition polymerization process appears to involve an initial absorption of the butadiyne in the substrate film followed by its thermal polymerization in the condensed phase. This is consistent with the observation that the polybutadiyne permeates the surface of the substrate film. The thermodynamic compatibility between the butadiyne monomer and substrate film appears to determine the order of polymerization selectivity, PVF2 > PE > PTFE > FEP. This order correlates with the solubility parameter match between butadiyne, 10.3 $(\text{cal/cm}^3)^{1/2}$, and the substrate films: PVF2, 8.4 $(\text{cal/cm}^3)^{1/2}$; PE, 8.0 $(\text{cal/cm}^3)^{1/2}$; PTFE, 6.2 $(\text{cal/cm}^3)^{1/2}$; FEP, < 6.2 $(\text{cal/cm}^3)^{1/2}$ [15]. The effect of butadiyne deposition polymerization on the x-ray diffraction patterns and DSC melting points indicates that an alteration of the crystalline regions of the substrate films is occurring in addition to penetration through the surface.

The objective of heat treating the vapor-deposited polybutadiyne samples was to induce useful electrical conductivity in a flexible plastic material by way of a chemical reaction analogous to that reported for a diphenyl-substituted butadiyne thermopolymer [2]. Although thermal reaction of the pendant acetylenic groups was observed, appreciable electrical conductivity was not measured within the 120 to 470°C heat treatment range. The postpolymerization thermal conversion of polyene structure (I) to polyacene structure (II) appears to be an oversimplification of the structure and reaction involved. Representation of the vapor-deposited polybutadiyne by the polyene structure is based on IR spectra interpretation [5c] and an analogy with previous diphenyldiacetylene thermal polymerization work [2]. Formation of the polyacene structure by intramolecular reaction of adjacent ethynyl groups would require a trans-polyene precursor of high repetitive regularity. In addition to the polyene repeat unit, other possible polybutadiyne linking structures consistent with the characterization data would include a minor amount of preformed polyacene or a trisubstituted benzoid linkage [5a, 5c]. The endgroup contribution could also be significant if, by analogy with the thermal polymerization of diphenyldiacetylene [2c], the polybutadiyne is oligomeric in molecular weight. The breath and unsymmetrical shape of the exotherm in the DSC thermogram (Fig. 2) may be indicative of side reactions consuming the pendant ethynyl groups. Exotherms in DSC thermograms of the cure of acetylene-terminated oligomers are much narrower, and model compound studies have shown that a complex distribution of oligomeric polyene and symmetrical and unsymmetrical benzoid trimer structures are possibly formed [18]. The polybutadiyne IR data are useful for monitoring the reaction of the acetylenic groups but are inconclusive as to the products formed. The ESR data, while difficult to draw structurally specific information from, are very similar to those obtained from pyrolytic carbon chars although the polybutadiyne heat treatment temperatures are much lower. Pyrrolytic carbons display the oxygen-pressure-dependent broadening of the ESR signal at heat treatment temperatures approaching 500°C [14] and do not develop appreciable electrical conductivities until a 900°C temperature is attained [19]. In summary, the heat-treated polybutadiyne appears to be a complex of carbon-rich aromatic structures more related to a pyrolytic carbon than to a structurally regular polyacene.

ACKNOWLEDGMENT

Dr Hank Wohltjen is gratefully acknowledged for the surface resistivity measurements.

REFERENCES

[1] G. Wegner, Makromol. Chem., 145, 85 (1971).

[2] (a) A. A. Berlin, M. I. Cherkashin, M. G. Chauser, and R. R. Shifrina, Vysokomol. Soedin., A9, 2219 (1967); (b) M. G. Chauser, M. I. Cherkashin, M. Ya. Kushnerev, T. I. Protsuk, and A. A. Berlin, Ibid., A10, 916 (1968); (c) M. G. Chauser, I. D. Kalikhman, M. I. Cherkashin, and A. A. Berlin, Ibid., A12, 1022 (1970).

[3] M. G. Chauser, I. D. Kalikhman, M. I. Cherkashin, and A. A. Berlin, Izv. Akad. Nauk SSSR. Khim., p. 2421 (1969).

[4] T. A. Kovacina, R. A. DeMarco, and A. W. Snow, Ind. Eng. Chem., Prod. Res. Dev., 22, 170 (1983).

[5] (a) A. W. Snow, Nature, 292, 40 (1981); (b) A. W. Snow, Carbon, 19, 467 (1981); (c) A. W. Snow, in New Monomers and Polymers (B. M. Culbertson and C. U. Pittman Jr., eds.), Plenum, New York, 1984, pp. 399-414.

[6] C. B. Duke and H. W. Gibson, in Encyclopedia of Chemical Technology, Vol. 18, Wiley, New York, 1982, pp. 755-794.

[7] J. L. Bredas, R. R. Chance, and R. H. Baughman, J. Chem. Phys., 76, 3673 (1982).

[8] J. B. Armitage and E. R. Jones, J. Chem. Soc., p. 44 (1951).

[9] A. V. Jones, Proc. R. Soc. London, A211, 285 (1952).

[10] K. K. Georgieff and Y. Richard, Can. J. Chem., 36, 1280 (1958).

[11] R. J. Tedeschi and A. E. Brown, J. Org. Chem., 29, 2051 (1964).

[12] Apparatus designed by Dr H. Wohltjen, NRL.

[13] A. W. Snow and J. R. Griffith, Polym. Prepr., 22(2), 389 (1981).

[14] L. S. Singer, Proceedings of the Fifth Carbon Conference, Vol. 2, Pergamon, New York, 1961, p. 37.

[15] (a) Butadiyne solubility parameter calculated from $\Delta H_V = 7761$ cal/mol and $d = 0.736$ g/cm^3 (CRC Handbook, 51 edition) at 293°K; (b) PE and PTFE solubility parameters calculated from Small's Molar Attraction Constants [16]; (c) PVF2 solubility parameter calculated from Small's Molar Attraction Constants [16] but the actual value is probably greater as indicated by high crystallite polarity and strong swelling by polar aprotic solvents [17]; (d) FEP solubility parameter is less than that of PTFE as indicated by correlation with critical surface tension [16, 17].

[16] J. L. Gardon, in Encyclopedia of Polymer Science and Technology, Vol. 3 (H. F. Mark, N. G. Gaylord, and N. M. Bikales, eds.), Wiley-Interscience, New York, 1965, pp. 855-857.

[17] M. K. Bernett and W. A. Zisman, J. Phys. Chem., 64, 1292 (1960).

[18] (a) P. M. Hergenrother, G. F. Sykes, and P. R. Young, Prepr., Div. Pet. Chem., Am. Chem. Soc., 24(1), 243 (1979). (b) M. D. Sefcik, E. O. Stejskal, R. A. Mckay, and J. Schaefer, Macromolecules, 12, 423 (1979).

[19] Y. Okamoto and W. Brenner, Organic Semiconductors, Reinhold, New York, 1964, pp. 91-93.

Accepted by editor June 3, 1984
Received for publication June 19, 1984