

Mechanism and Kinetics of Stabilization Reaction of Polyacrylonitrile and Related Copolymers I. Relationship between Isothermal DSC Thermogram and FT/IR Spectral Change of an Acrylonitrile/Methacrylic Acid Copolymer

Hideto KAKIDA[†], Kohji TASHIRO,* and Masamichi KOBAYASHI*

Central Research Laboratories, Mitsubishi Rayon Co., Ltd., Otake, Hiroshima 739-06, Japan

* Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan

(Received August 23, 1995)

ABSTRACT: Intimate relationship between the thermal behavior and the structural change has been clarified for the first time by an organized combination of isothermal DSC thermogram and FT/IR spectra measured for the stabilization reaction of an acrylonitrile (AN)/methacrylic acid (MAA) copolymer. In an early stage of the isothermal exothermic thermogram measured by DSC under air, a flat region or the induction period of the cyclic structure formation was found to exist, which is immediately followed by the two stages of steep heat evolution and the slow heat release. Based on the IR spectral changes observed during this thermal reaction, the induction stage was found to be associated with the reaction of methacrylic acid groups with the adjacent nitrile groups and the steep heat evolution region with the propagation of the cyclic structure and dehydrogenation of the polyacrylonitrile (PAN) chain sequences to give an unsaturated ladder structure. An activation energy for this initiation reaction of the cyclic structure formation was evaluated to be *ca.* 26 kcal/mol by an Arrhenius plot.

KEY WORDS Polyacrylonitrile / Methacrylic Acid / DSC / FT/IR / Precursor / Carbon Fiber / Stabilization / Induction Period /

Polyacrylonitrile (PAN) containing acidic comonomers are the most commonly used precursors for carbon fibers because of the excellent performance of PAN based carbon fibers.¹

Production process of PAN based carbon fibers involves a stabilization of oriented acrylic fibers and a carbonization of them at elevated temperature.² Stabilization is the most important process which converts PAN to an infusible and nonflammable fiber by heating at 200–300°C for about one hour in an oxidative atmosphere. Thus stabilized fibers can be heated up to carbonization temperature (1000–2000°C) in an inert gas atmosphere.²

A number of studies^{5–28} have been reported concerning the stabilization of PAN since the proposition of the fully hetero aromatic cyclic structure for the stabilized PAN in 1950.⁴ The subject of stabilization was reviewed by Bashir 40 years after this first proposition.³

PAN copolymers containing acidic comonomers work as a good precursor and gives high quality carbon fibers. The role of comonomers in the stabilization reaction was said to lower the initiation temperature of cyclization reaction.¹ Grassie and coworkers^{27,28} studied by DTA method the effects of some comonomers on lowering the stabilization temperature. Some acidic comonomers, *e.g.*, itaconic acid, methacrylic acid (MMA), and acrylic acid, lower the exothermic peak temperature and also decrease the peak height in the following order:

itaconic acid > methacrylic acid > acrylic acid
> acrylamide

In this way the degree of reduction of the exothermic peak temperature may be useful as a measure of the effect of comonomers in stabilization reaction.

On the other hand, the effects of comonomers on the

kinetic behavior of PAN copolymers have been studied only by a few groups.^{28–37} Noh *et al.* and other groups measured the rate of decrease of nitrile concentration during heat treatment.^{28,32–35} Uchida *et al.*²⁹ and Watt and Johnson³¹ measured the rate of oxygen uptake during isothermal oxidation of acrylonitrile (AN) copolymers in air. Fitzer³⁰ obtained the activation energies of thermooxidative reaction of PAN and AN copolymers from the DTA data based on the Kissinger method.³⁸ Collins *et al.*^{36,37} developed a kinetic model including the two rate processes so as to simulate the heat flow behavior occurring in the isothermal DSC thermogram.

As stated above, many studies on the stabilization of PAN have been done in these 45 years, but all of the proposed stabilization mechanisms are only hypotheses without any experimental confirmation.³ There have been also very few kinetic studies which could evaluate the comonomer's stabilization promoting ability. In order to clarify the kinetics and mechanism of the stabilization of PAN and related copolymers, we have developed a new idea to combine the experimental data of isothermal DSC thermogram and FT/IR spectra. Through this study we have found that there exists an induction period in the DSC thermogram of the AN copolymer when it is measured isothermally in air. The FT/IR measurement revealed that this induction period involves the reaction of comonomer units with adjacent nitrile groups, which is immediately followed by the cyclization of nitriles and the steep dehydrogenation of the PAN chain sequences. The observation of such an induction period for PAN stabilization reaction may be the first as long as the authors know in the literatures. The induction period should give a basis for the kinetic study of stabilization of PAN through the isothermal DSC measurements as discussed in the present paper.

[†] To whom all correspondence should be addressed.

EXPERIMENTAL

Materials

An acrylonitrile copolymer which contains about 1 mol% methacrylic acid was obtained by aqueous suspension polymerization method with redox initiator. The weight averaged molecular weight was about 2×10^5 . The polymer powders filtered through a 400 mesh screen were employed for the DSC and FT/IR measurements.

DSC Measurement

The DSC measurements were carried out by using a SEIKO DSC 220C controlled by a thermal analyzer SSC 5000 system. Sample of 4mg was found to be the best among 1–10 mg because the accumulation of heat was the least and the polymer powders were evenly dispersed in an Al pan. The polymer powders were sealed in an Al pan with a mesh cover to allow air diffusion into powders. Isothermal DSC thermograms were measured at several constant temperatures between 170–250°C.

FT/IR Measurements

The JASCO FT/IR 7300 was used at a resolution of 4 cm^{-1} to detect the structural changes during the isothermal exothermic reactions observed in DSC thermograms. The IR measurements were made for the KBr disks (1 mg sample with 200 mg KBr) for the specimens treated thermally in DSC cell for predetermined periods.

RESULTS AND DISCUSSION

Isothermal DSC Measurements

Figure 1 shows the isothermal DSC thermograms measured at various temperatures under air flow for the AN copolymer, which contains about 1 mol% methacrylic acid. At higher temperature, the exothermic peak becomes sharper and shifts to the side of shorter time.

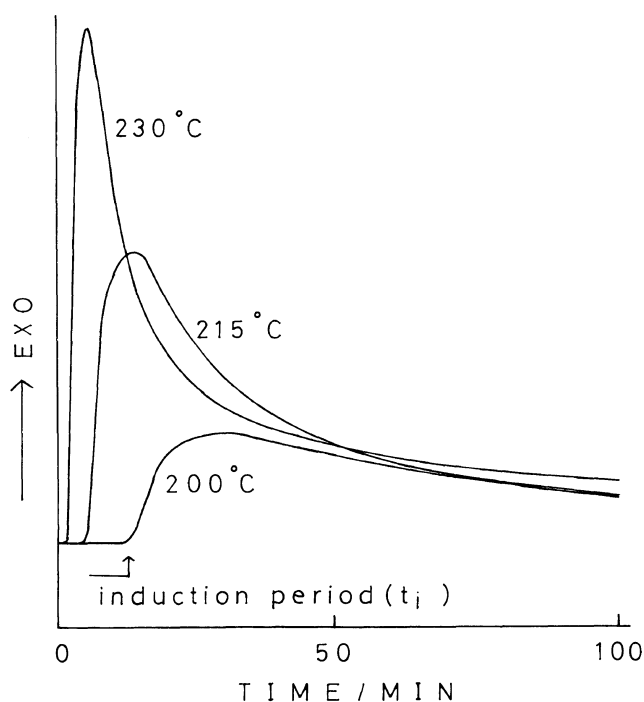


Figure 1. Isothermal DSC thermograms of the AN/MAA copolymer measured at several temperatures under air flow.

That is to say, the stabilization reaction rate is faster at higher temperature. In the DSC thermogram of Figure 1, in addition to this large exothermic peak one can see a flat region at an early stage between 0 to 15 min. The period of the flat region appears to become shorter as the temperature increases. Immediately after this flat region, an abrupt heat evolution is observed. Therefore this flat region may be assumed to be an induction period for the main thermal reaction. In Figure 2, the Arrhenius plot is made for the induction periods obtained at 170, 190, 210, and 230°C, where the induction period t_i is defined as the standing point of the steep thermal evolution (see Figure 1). From this plot an activation energy evaluated as *ca.* 26 kcal mol^{-1} .

Structure Changes during Exothermic Reactions

The molecular structural changes of the copolymer along the isothermal exothermic DSC thermogram were investigated by means of FT/IR. In Figure 3, a typical DSC thermogram measured isothermally is illustrated. The exothermic phenomena are not very simple but are composed of several stages; an induction period, an exothermic shoulder and an exothermic main peak as indicated in this figure. The IR spectra were measured

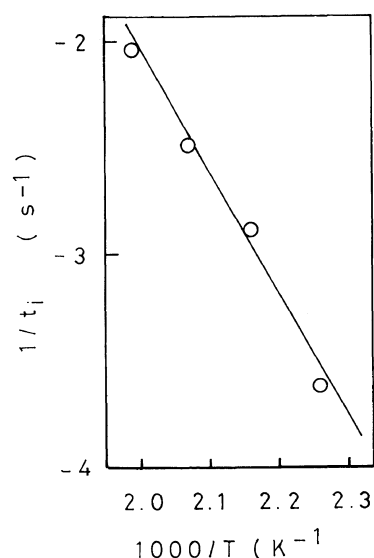


Figure 2. The Arrhenius plot of the induction period (t_i) measured at 170, 190, 210, and 230°C.

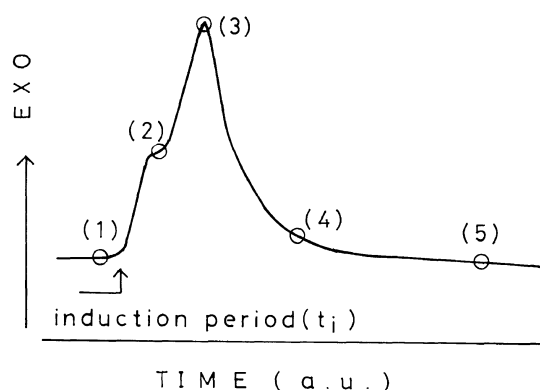


Figure 3. The schematic DSC thermogram of the AN/MAA copolymer measured at 230°C under air. The (1)–(5) indicate the points where the IR spectra were observed as shown in Figure 4.

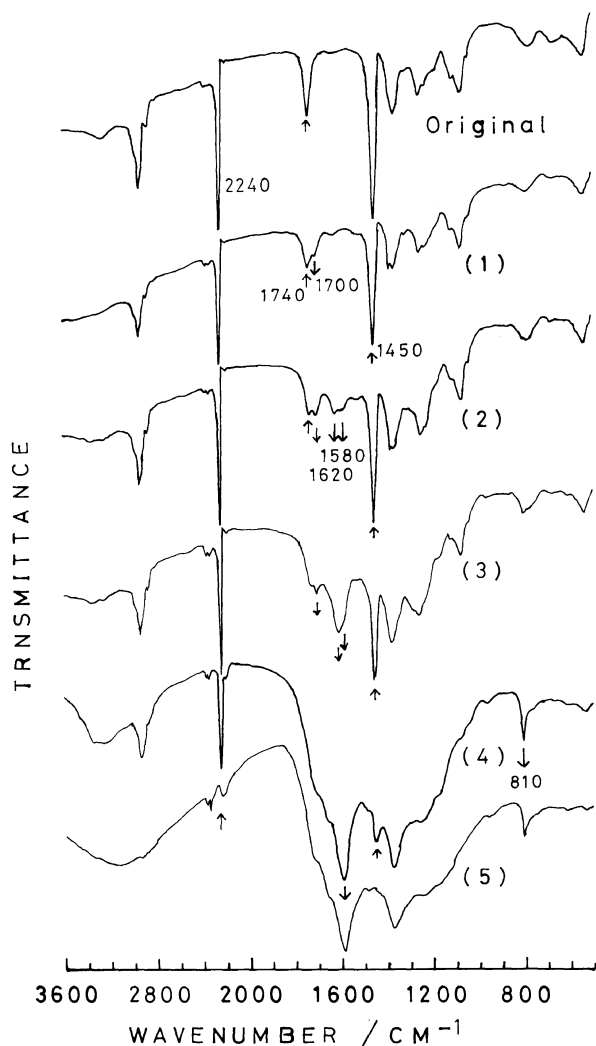


Figure 4. The IR spectra of the AN/MAA copolymer which were observed at points (1)–(5) shown in Figure 3.

preliminarily at the points (1)–(5) illustrated in Figure 3 to investigate roughly the structural changes occurring in the DSC thermogram. The spectra are shown in Figure 4. One can see that the bands at 2240, 1740, and 1450 cm^{-1} decrease in intensity while the bands at 1700, 1620, 1580, and 810 cm^{-1} increase the intensity as the IR measurement proceeds from (1) to (5). In Figure 5, the isothermal DSC thermogram and the changes of the several main IR band intensities are shown in the same time scale. One can see that the IR band intensities change drastically in the remarkable exothermic region of 0 to 50 min, the bands at 1600, 810 cm^{-1} increase in intensity while the bands at 2240, 1450 cm^{-1} decrease in intensity. In Figure 6, the early stage of isothermal DSC thermogram measured at 230°C in air is shown together with the corresponding time dependence of the IR band intensities measured at shorter time interval. In the early flat region [I] or an induction period, the 1740 cm^{-1} band intensity decreases and the 1700 cm^{-1} band begins to appear and increases its intensity with time, but the 2240 and 1450 cm^{-1} bands show no intensity changes. In the region [II], where the rapid heat release occurs, the 2240 cm^{-1} nitrile band and the 1450 cm^{-1} methylene band begin to decrease their intensities. The 1620 and the 1580 cm^{-1} bands begin to appear in this region and

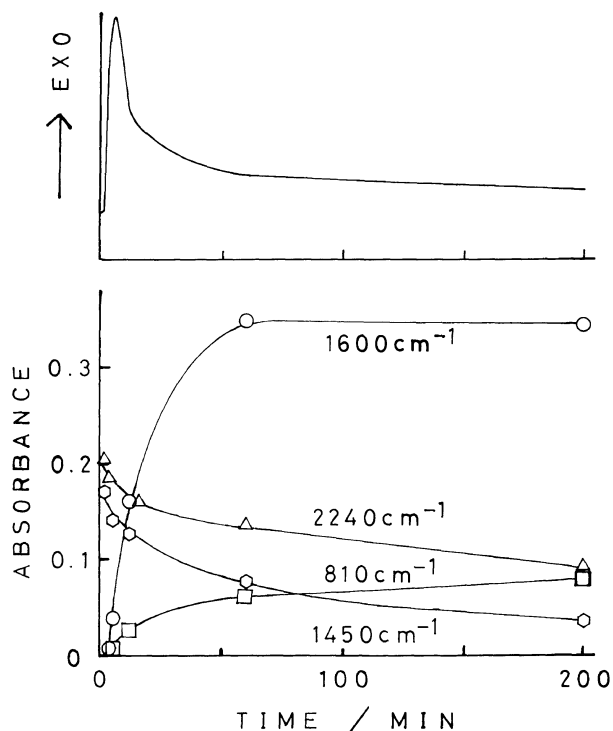


Figure 5. A comparison of the isothermal DSC thermogram with the intensity changes of the main IR bands.

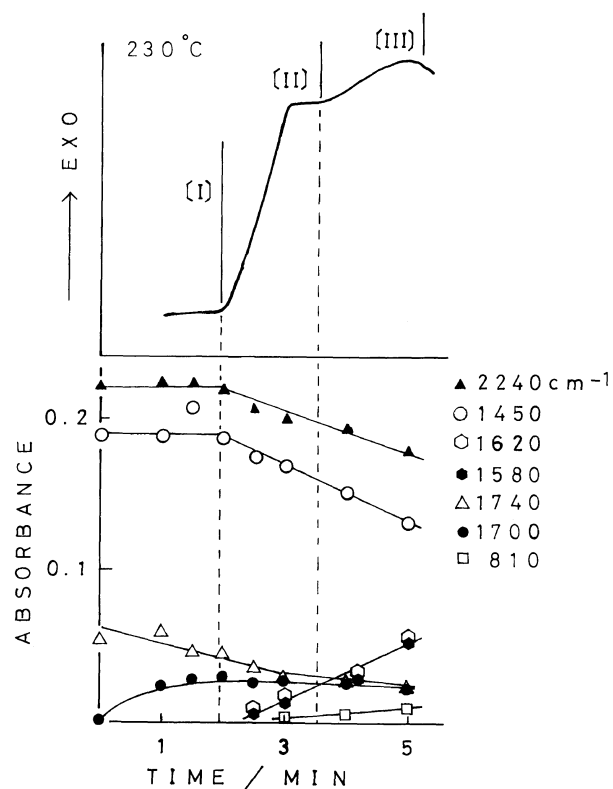


Figure 6. The early region of isothermal DSC thermogram measured at 230°C and the corresponding changes of the intensity of the several main IR bands.

increase the intensities. After this rapid heat release, the second flat appears in the later stage of [II]. In this region, the 810 cm^{-1} band begins to appear. In the exothermic peak region [III], the 2240 and 1450 cm^{-1} bands continue to decrease and the 1620, 1580, and

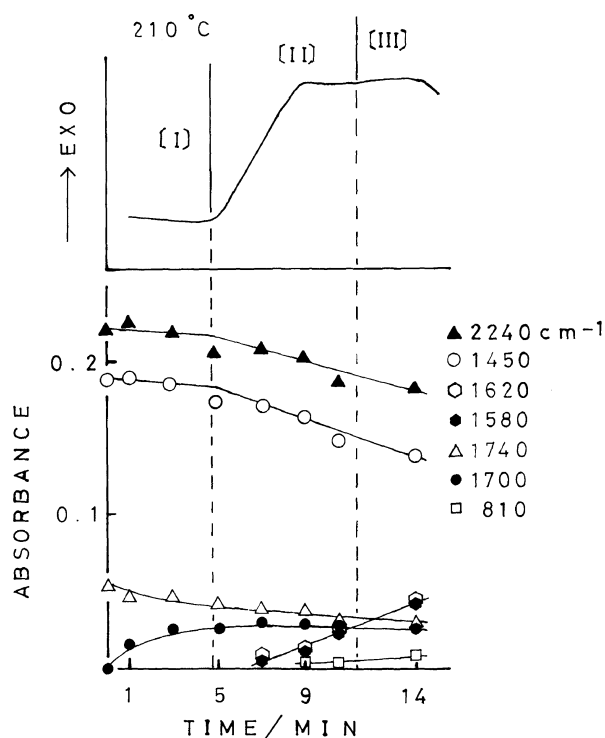


Figure 7. The early region of isothermal DSC thermogram measured at 210°C and the corresponding changes of the intensity of the several main IR bands.

Table I. Principal IR bands in solid and degraded AN/MAA copolymer structures

Functional groups	Wavenumbers/cm ⁻¹
NH ₂	3390, 3356
NH	3230
CH ₂	2945, 2920 (2930)
CH	2895
C≡N (saturated)	2240
C=O (unreacted MAA)	1740
C=O (reacted MAA)	1700
C=N, C=C mixed	1620 ^a
C=N, C=C, (NH) mixed	1580 ^a
CH ₂	1450
CH, NH	1380
C-C, C-N mixed	1250
C=C-H	810

^a These bands are often not resolved and appear at $1600 \pm 10 \text{ cm}^{-1}$.

810 cm⁻¹ bands increase their intensities. In Figure 7, the results obtained at 210°C is shown. The correspondence between the DSC thermogram and the IR spectral change is essentially the same for both the measurements shown in Figures 6 and 7. But the time required for the heat-release chemical structural changes becomes longer as the treatment temperature is decreased.

Table I summarizes the IR band assignments for the degraded PAN with reference to the reports by Fochler *et al.*³⁴ and Sivy *et al.*³⁹ The chemical structural changes which occur in the early stage of the stabilization of AN/MAA copolymer are shown in Figure 8 which is illustrated in accordance with Sivy *et al.*³⁹ and Fitzer.³⁰ With reference to Table I and Figure 8, the phenomena observed in Figures 6 and 7, *i.e.*, the heat release phenomena in isothermal DSC thermogram and the IR spec-

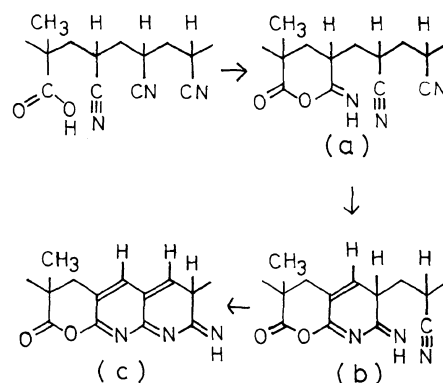


Figure 8. The chemical structural changes which occur in the early stage of the stabilization of AN/MAA copolymer.

tral changes may be interpreted as follows.

According to Sivy *et al.*,⁴⁰ the 1740 cm⁻¹ C=O stretching band of methacrylic acid residue of the untreated PAN copolymer shifts to 1700 cm⁻¹ when the carboxyl group forms a cyclic structure (a) of Figure 8 through the reaction with an adjacent nitrile group. The intensity changes of these two bands observed in Figures 6 and 7 are considered to correspond to this reaction. In other words, this type of cyclization is considered to occur in the induction period of the DSC thermogram. The thus constructed ring structure seems to work as a nucleus for the further propagation reaction of the ring structure. In the next heat release region [II], the propagation of ring structure (structure (b) of Figure 8), *i.e.*, the cyclization and the dehydrogenation start to occur, as supported by the decrease of the C≡N (2240 cm⁻¹) and CH₂ (1450 cm⁻¹) band intensities and the increase of the C=C and C=N (1580, 1620 cm⁻¹) bands. In the second flat region of the stage [II], the C=C-H (810 cm⁻¹) band appears and continues to grow (structure (c) of Figure 8). After passing the main peak [III], the heat release rate slows down and at the same time the C≡N and CH₂ bands become weak gradually and disappear at last. The C=C, C=N bands and the C=C-H band grow up slowly and become saturated soon.

In this way, the combination of isothermal DSC thermogram with IR spectra was found to be very useful for clarifying the intimate relationship between the thermal behavior and the structural change occurring in the stabilization process of PAN.

The IR spectral data revealed the following reaction scheme for the isothermal heat treatment of PAN and the copolymer. At first, during the induction period, some amounts of carboxyl groups of MAA form the cyclic structures with adjacent nitrile groups. This cyclic structure propagates to the larger structure through the nitrile oligomerization and the dehydrogenation with steep heat evolution, although it is not clear even now which reaction goes ahead, the nitrile oligomerization or the dehydrogenation. After passing the exothermic peak of the DSC thermogram, both the reactions slow down.

REFERENCES

1. A. Gupta, D. K. Paliwal, and P. B. Jaj, *J. Macromol. Sci.*, 1 (1991).
2. J. B. Donnet and R. C. Bansal, "Carbon Fiber," 2nd. ed, Marcel Dekker, New York, N.Y., 1990.

3. Z. Bashir, *Carbon*, **29**(8), 1081 (1991).
4. R. C. Houtz, *Textile Res. J.*, **20**, 786 (1950).
5. N. Grassie, J. N. Hay, and I. C. McNeill, *J. Polym. Sci.*, **31**, 205 (1958).
6. W. J. Burlant and J. L. Parsons, *J. Polym. Sci.*, **22**, 249 (1956).
7. E. M. LaCombe, *J. Polym. Sci.*, **24**, 152 (1957).
8. J. Schurz, *J. Polym. Sci.*, **28**, 438 (1958).
9. N. Grassie and J. N. Hay, *J. Polym. Sci.*, **56**, 189 (1962).
10. T. Takata, I. Hiroi, and N. Taniyama, *J. Polym. Sci., A*, **2**, 1567 (1964).
11. R. T. Conley and J. F. Bieron, *J. Appl. Polym. Sci.*, **7**, 1757 (1963).
12. A. A. Berlin, A. M. Dubinskaya, and Y. S. Moscovskii, *Polym. Sci. USSR*, **6**, 2145 (1965).
13. W. Fester, *Textile Rundschau*, **20** (5), 1 (1965).
14. W. Fester, *J. Polym. Sci., C*, **16**, 755 (1965).
15. N. Grassie and R. McGuchan, *Eur. Polym. J.*, **7**, 1091 (1971).
16. N. Grassie and R. McGuchan, *Eur. Polym. J.*, **7**, 1357 (1971).
17. N. Grassie and R. McGuchan, *Eur. Polym. J.*, **7**, 1503 (1971).
18. L. H. Peebles and J. Brandrup, *Makromol. Chem.*, **98**, 189 (1966).
19. A. E. Standage and R. D. Matkowsky, *Eur. Polym. J.*, **7**, 775 (1971).
20. A. Clarke and J. Bailey, *Nature*, **234**, 529 (1971).
21. W. D. Potter and G. Scott, *Nature*, **236**, 30 (1972).
22. W. Watt, D. J. Johnson, and E. Parker, "Proceedings of the International Conference on Carbon Fiber," The Plastic Institute, London, 1974, p 3.
23. G. T. Sivy and M. M. Coleman, *Carbon*, **21**, 573 (1983).
24. G. H. Olive and S. Olive, *Polym. Bull.*, **5**, 457 (1981).
25. T. Takahagi, I. Simada, M. Fukuhara, K. Morita, and A. Isitani, *J. Polym. Sci., Polym. Chem. Ed.*, **24**, 3101 (1986).
26. N. Grassie and R. McGuchan, *Eur. Polym. J.*, **8**, 257 (1972).
27. N. Grassie and R. McGuchan, *Eur. Polym. J.*, **8**, 865 (1972).
28. I. Noh and H. Yu, *J. Polym. Sci., B*, **4**, 721 (1966).
29. T. Uchida, I. Shionoya, K. Terada, and K. Nukada, *Polym. Prepr., Jpn.*, **20**, 116 (1971).
30. E. Fitzer and D. J. Muller, *Carbon*, **13**, 63 (1975).
31. W. Watt and W. Johnson, *Nature*, **257**, 210 (1975).
32. M. M. Coleman and R. J. Petcavich, *J. Polym. Sci., Polym. Phys. Ed.*, **16**, 821 (1978).
33. M. M. Coleman and G. T. Sivy, *Carbon*, **19**, 123 (1981).
34. H. S. Fochler, J. R. Mooney, L. E. Ball, R. D. Boyer, and J. G. Grasseli, *Spectrochimica Acta*, **41A**(1/2), 271 (1985).
35. I. Simada, T. Takahagi, K. Morita, and A. Isitani, *J. Polym. Sci., Polym. Chem. Ed.*, **24**, 1989 (1986).
36. G. L. Collins, N. W. Thomas, and G. E. Williams, *Fiber Sci. Technology*, **20**, 37 (1984).
37. G. L. Collins, N. W. Thomas, and G. E. Williams, *Carbon*, **26**, 67 (1988).
38. H. E. Kissinger, *Anal. Chem.*, **29**, 1702 (1957).
39. G. T. Sivy and M. M. Coleman, *Carbon*, **19**, 127 (1981).