(6) Sato, H.; Takebayashi, K.; Tanaka, Y. *Macromolecules* **1987**, *20*, 2418.
(7) Sato, H.; Tanaka, Y.; Taketomi, T. *Makromol. Chem.* **1977**, *178*, 1993.
(8) Tanaka, Y.; Sato, H.; Hatada, K.; Terawaki, T.; Okuda, H. *Makromol. Chem.* **1977**, *178*, 1823.
(9) Wall, L. A.; Brown, D. W. *J. Phys. Chem.* **1957**, *61*, 129.
(10) Sato, H.; Tanaka, Y. *ACS Symp. Ser.* **1984**, *247*, 181.
(11) Sato, H.; Tanaka, Y. *Macromolecules* **1984**, *17*, 1964.
(12) Ogawa, M.; Sato, H.; Tanaka, Y., unpublished data.
(13) Pegg, D. T.; Doddrell, D. M.; Bendall, M. R. *J. Chem. Phys.* **1982**, *77*, 2745.

Photocross-Linking in a Magnetic Field: Behavior of a Poly(styrene-*co*-butadiene) Containing Ketones or Covalently Bound Keto Groups

Michael G. Martl, Raimund Schaller, and Klaus Hummel*

Institut für Chemische Technologie organischer Stoffe, Technische Universität Graz,
Stremayrgasse 16, A-8010 Graz, Österreich, Austria.

Received January 4, 1988; Revised Manuscript Received June 2, 1988

ABSTRACT: A poly(styrene-*co*-butadiene) (SBR) was photocross-linked in the presence of various ketones at 20 °C. The degree of cross-linking was determined by sol/gel analysis. The cross-linking efficiency increased in the order deoxybenzoin, benzophenone, dibenzyl ketone, *p*-methylbenzophenone. For comparison, the SBR was modified with phenylacetyl chloride, whereby phenylacetylphenyl groups were formed, and then photocross-linked in the absence of additives; the cross-linking efficiency was relatively low. Experiments were carried out without magnetic field and with external homogeneous magnetic fields between 42 and 975 mT. Even low-flux densities (42 mT) brought about a definite effect. The magnetic field effect reached its highest value at about 240 mT in all experiments. The smallest influence of the magnetic field was observed for the SBR with phenylacetylphenyl groups. The results are discussed using radical pair theory.

Introduction

Photoreactions in a polymer matrix are of interest to modern science and technology for photoprocesses (e.g., "microlithography"), optical memory systems, or solar energy conversion.[1] They are also important for the theory of energy transfer, migration in polymers, and segment mobility.[2-4] The present paper is concerned with photocross-linking in an external magnetic field.

Interest in the investigation of chemical reactions in magnetic fields has grown in recent years. The difference in the results (e.g., product yields or cross-linking densities) received without and with the influence of a magnetic field can be denoted "magnetic field effect". In the following, we only consider reactions with radical intermediates. The magnetic field effect can here be interpreted by the radical pair theory, which is also the theoretical background of CIDNP spectroscopy.[5]

Most investigations describing magnetic field effects have been concerned with low molecular chemistry, for example, photochemical reactions in micellar solutions, in particular the photolysis of ketones.[6,7] Some work in polymer chemistry has also been published. First, the cross-linking of 1,4-polybutadiene by photolysis of peroxides in the presence of phenanthrene was investigated in the magnetic field.[8] Second, the influence of a magnetic field on photocross-linking of bromo- and chloromethylated polystyrene in the presence of thioxanthone was described.[9] Third, a magnetic field effect was found in the photocross-linking of a poly(styrene-*co*-butadiene) (SBR) in the presence of ketones such as deoxybenzoin.[10] The keto groups were covalently linked to the polymer chain in additional experiments.[11] The photocross-linking yield increased in a magnetic field (in contrast to cross-linking of 1,4-polybutadiene with bis(2,4-dichlorobenzoyl) peroxide[8,12,13]). For example, 15-20% more cross-linking (measured by sol/gel analysis) was found with dispersed ketones and 3-10% more cross-linking for the copolymer with keto groups at a flux density B of 1.0 T.

The magnetic field effect, plotted as a function of the flux density (B), at the beginning increases with B and seems normally to attain a constant value at relatively low magnetic fields.[9,12] But the absolute value can also pass a maximum at a certain value of B. Experimental examples are provided by the (Z)-(E) photoisomerization of stilbene[14] and the photolysis of *p*-chlorodibenzyl ketone or 1,2-diphenyl-2-methylpropanone.[15]

In the present investigation, the flux density dependence of the magnetic field effect on the photocross-linking of copolymer/ketone systems is described for the first time. On the one hand, an SBR was cross-linked in the presence of deoxybenzoin ($C_6H_5CH_2COC_6H_5$), benzophenone ($C_6H_5COC_6H_5$), dibenzyl ketone ($C_6H_5CH_2COCH_2C_6H_5$), or *p*-methylbenzophenone ($CH_3C_6H_4COC_6H_5$). On the other hand, the SBR was modified by Friedel-Crafts reaction of the phenyl groups of the copolymer with phenylacetyl chloride and then photocross-linked; this polymer contained phenylacetylphenyl groups ($C_6H_5CH_2COC_6H_4$–) which correspond to deoxybenzoin.

Experimental Section

Materials. The SBR was supplied by Goodyear (SBR-E-3024, 10 wt % styrene). It was purified from a solution in methylene chloride by precipitation with methanol. The ketones used were commerical products (p.a.) of Fluka without further purification.

For photocross-linking, a solution of 2 wt % copolymer in methylene chloride was prepared. The ketone was added and dissolved. Then the solvent was evaporated and the remaining mixture vacuum-dried and kept in the dark at 5 °C.

The copolymer with covalently bound phenylacetylphenyl groups was received by reaction of the SBR with phenylacetyl chloride as described previously.[11]

Photocross-Linking. Polymer foils (thickness 25 μm) were received by pressing 2 mg of the copolymer/ketone mixture or the copolymer with phenylacetylphenyl groups between two glass plates. The foils were fixed to a thermostated (20 °C) aluminum block positioned between the poles of the electromagnet (Bruker BE 10/B-Z 11ha) and irradiated with a 150-W high-pressure mercury lamp (Hanau TQ 150) at a distance of 80 cm.[10] All

0024-9297/89/2222-1753$01.50/0 © 1989 American Chemical Society

Table I
Sol/Gel Analysis of Photocross-Linked SBR,[a] Magnetic Field Dependence

	(a)			(b)		
B, mT	$\bar{G}$, %	s, %	P	$\bar{G}$, %	s, %	P
0	21.78	1.78		69.18	0.78	
42	20.61	1.13	80.0–90.0	67.70	0.70	97.5–99.0
90	19.99	1.56	80.0–90.0	67.38	0.60	99.5–99.9
139	19.53	0.68	90.0–95.0	66.31	1.01	99.0–99.5
240	19.17	1.46	90.0–95.0	64.63	0.69	>99.9
390	19.03	0.35	95.0–97.5	64.78	0.82	>99.9
600	18.90	1.11	95.0–97.5	65.46	0.84	99.5–99.9
780	18.84	1.29	95.0–97.5	64.83[b]	2.09	

[a] Mixture of SBR with deoxybenzoin (10 mmol/100 g of copolymer) and (b) SBR containing phenylacetylphenyl groups (10 mmol/100 g of copolymer); irradiation time 30 min. [b] Mean of two values.

Table II
Sol/Gel Analysis of Photocross-Linked SBR,[a] Magnetic Field Dependence

	(a)			(b)			(c)		
B, mT	$\bar{G}$, %	s, %	P	$\bar{G}$, %	s, %	P	$\bar{G}$, %	s, %	P
0	55.78	0.80		54.87	0.69		52.64	0.76	
42	54.60	1.75	80.0–90.0	50.46	0.82	>99.9			
90	53.38	1.66	95.0–97.5	47.14	0.74	>99.9	47.63	1.70	99.5–99.9
139	51.09	0.60	>99.9	48.06	2.28	99.5–99.9			
240	48.36	0.79	>99.9	46.36	1.42	>99.9	44.71	1.50	>99.9
390	48.96	1.46	99.5–99.9	46.88	0.23	>99.9			
600	49.97	0.87	>99.9	47.01	1.81	>99.9	44.89	1.97	99.5–99.9
780	48.21	1.09	>99.9	46.97	1.30	>99.9			
975	48.42	0.28	>99.9	47.91	1.00	>99.9	45.15	0.95	>99.9

[a] Mixture with (a) benzophenone, (b) dibenzyl ketone, and (c) p-methylbenzophenone (10 mmol of ketone/100 g of polymer); irradiation time 10 min.

inadequacies of the experimental setup (for example, the possible influence of the field on the mercury lamp) were excluded as described previously.[8,10]

Sol/Gel Analysis. The cross-linked foils were removed from the glass plates and weighed (G_v). They were then extracted with 15 mL of toluene for 3 days at 20 °C. The remaining gel was dried for 24 h at 40 °C and 16 Torr and weighed (G_n). From this, the soluble fraction G (%) = $(G_v - G_n)100/G_v$ was determined. The cross-linking degree of the polymer increases with decreasing G.

Results

Table I shows the data concerning (a) a mixture of the SBR with deoxybenzoin (10 mmol/100 g of copolymer) and (b) the SBR containing phenylacetylphenyl groups (10 mmol/100 g of copolymer). The irradiation time was 30 min. Photocross-linking was performed at flux densities B = 42, 90, 139, 240, 390, 600, and 780 mT. Experiments were not carried out in this order, but at random (for example, in the sequence 139, 42, 600, 390, 240, 90, 780 mT) to achieve random distribution of experimental errors due to unavoidable small changes in the experimental setup. The mean $\bar{G}$ of the results of three separate determinations of G was calculated for each value of B. A comparison of the $\bar{G}$ values in (a) and (b) demonstrates that the copolymer/ketone mixture is more cross-linked than the modified copolymer under the same experimental conditions.

A statistical evaluation of the G values was carried out, see Table I; s is the standard deviation and P is the significance level according to Student's t-test.[16] P is the probability that the G values for the given flux density do not belong to the same parent distribution as the G values for B = 0.

In the following, the values of $\bar{G}$ at $B \neq 0$ (denoted G_B) are compared with the values of $\bar{G}$ at B = 0 (denoted G_0). The relative differences E (%) = $(G_B - G_0)100/G_0$, calculated from the $\bar{G}$ values in Table I (a) and (b), are plotted versus B in Figure 1. In the case of the copolymer with phenylacetylphenyl groups, the E values are only about 50% of those received for the mixture of the copolymer with deoxybenzoin. The most recognizable changes are observed in the range B = 0–240 mT.

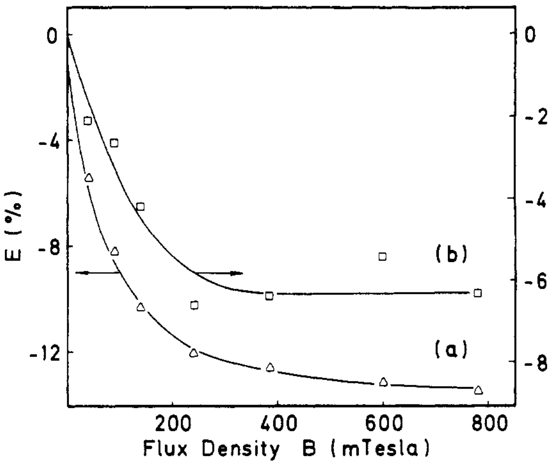


Figure 1. Magnetic field effect (E) in photocross-linking of (a) SBR with deoxybenzoin (10 mmol/100 g of copolymer) and (b) SBR containing phenylacetylphenyl groups (10 mmol/100 g of copolymer) at different magnetic flux densities (B); irradiation time 30 min.

Table II shows the corresponding results, with additional measurements at 975 mT, for the mixtures of the SBR with (a) benzophenone, (b) dibenzyl ketone, and (c) p-methylbenzophenone (10 mmol of ketone/100 g of copolymer). The irradiation time was 10 min. Photocross-linking was carried out as described above. As Figure 2 shows, all three systems have dependences of E on the flux density (B) similar to those in Figure 1. A steep increase in the effect is observed up to B = 240 mT. At higher fields, E remains constant within experimental error.

With regard to the cross-linking efficiency and the magnitude of the magnetic field effect, the results received with benzophenone can be compared with those published previously for the same SBR containing benzoylphenyl groups ($C_6H_5COC_6H_4$–).[11,17] The magnetic field effect is

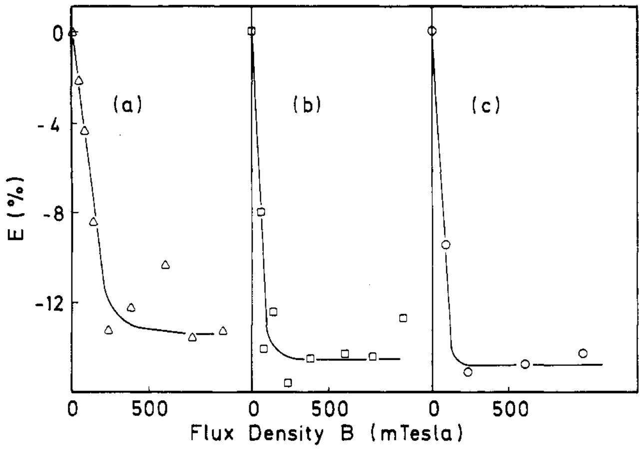


Figure 2. Magnetic field effect (E) in photocross-linking of SBR with (a) benzophenone, (b) dibenzyl ketone, and (c) p-methylbenzophenone (10 mmol of ketone/100 g of copolymer) at different magnetic flux densities (B); irradiation time 10 min.

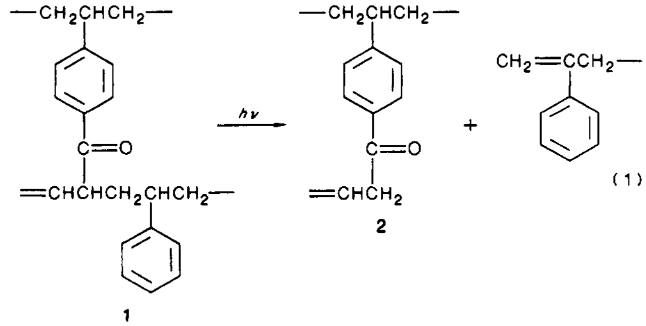
higher in the case of the mixture of the copolymer with benzophenone (up to 13%) than for the copolymer containing benzoylphenyl groups (about 5%). This is the same tendency as in Table I and Figure 1 for the mixture of the SBR with deoxybenzoin and the copolymer containing phenylacetylphenyl groups. But in contrast to the data in Table I, cross-linking efficiency with respect to the keto groups is much higher in the case of the copolymer containing benzoylphenyl groups than in the mixture of the SBR with benzophenone.[11]

Discussion

A. Cross-Linking Efficiencies. An interesting point in the results is the difference in cross-linking efficiencies of SBR/ketone mixtures and SBR modified with corresponding amounts of keto groups. Though this investigation gives no direct insight into the mechanisms, this can be explained by differences in the reaction pathways.

1. Deoxybenzoin and Phenylacetylphenyl Groups. The main reaction in photolysis of deoxybenzoin is α-cleavage.[18] A radical pair of a benzyl radical ($C_6H_5CH_2^\bullet$) and a benzoyl radical ($C_6H_5CO^\bullet$) is formed in the first step. Besides other reactions, these radicals abstract H atoms from the SBR chains. Among other possibilities, cross-links are the result of the combination of two macroradicals ($-CH_2\dot{C}HCH{=}CH-$).

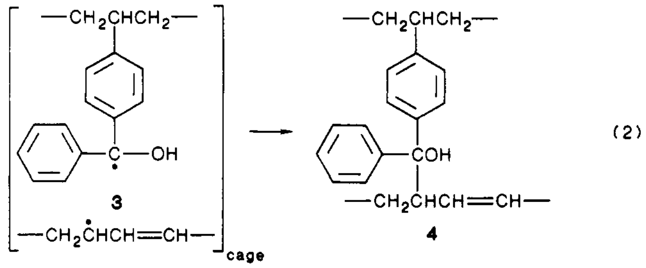
In the case of SBR containing phenylacetylphenyl groups, a radical pair of a benzyl and a macrobenzoyl radical ($-CH_2CH(C_6H_4CO^\bullet)CH_2-$) is formed by α-cleavage. Again H abstraction is among the following reaction steps. But the combination of macrobenzoyl radicals with macroradicals yields unstable cross-links, 1, which may undergo chain scission;[19] see eq 1. The resulting ketone, 2, may be once more subject to α-cleavage and so on. This provides an explanation for the lower cross-linking efficiency observed.



(1)

2. Benzophenone and Benzoylphenyl Groups. The photocross-linking of the mixture SBR/benzophenone proceeds via reaction between benzophenone and a polymer chain as an H donor (photoreduction[20,21]). A radical pair consisting of a ketyl radical ($(C_6H_5)_2\dot{C}-OH$) and a macroradical results. The free ketyl radical may react under abstraction of an H atom from another polymer chain to form a further macroradical. One possibility for cross-linking is the combination of two macroradicals.

In the case of the SBR containing benzoylphenyl groups, the initially formed radical pair consists of a macroketyl radical, 3, and a macroradical; see eq 2. In contrast to the mixture SBR/benzophenone, a recombination of the radical pair yields a cross-link, 4. This explains the higher cross-linking efficiency of the modified polymer compared with the mixture.



(2)

B. Field Dependence. For a qualitative interpretation of our experimental results, a short survey of some assumptions of the radical pair theory may be useful.[5] The ratio of cage-to-escape products depends on the relative spin orientation of the components of the radical pair. Cage products result mainly from singlet (S), escape products from triplet (T). For radical pairs, the exchange energy is small, and therefore, S–T crossing is possible. There are two mechanisms for S–T crossing. **(a) hfi Mechanism.** The spins of the radical pair may change their relative orientations by hyperfine interaction (hfi). The singlet S and the triplet sublevels T_0, T_+, and T_- are at about the same energy without external magnetic field. The rate of S–T crossing is the same for all sublevels. In the presence of an external field, S remains degenerate with T_0. But T_+ and T_- do not lie at the same energy level as T_0. The rate of S–T crossing is decreased in the field. **(b) Δg Mechanism.** S–T_0 transitions can also be induced by a difference in the g values of the components of the radical pair (Δg). Here the rate of S–T_0 crossing is increased proportional to the applied field strength and Δg. The Δg mechanism counteracts the hfi mechanism, and a maximum of the magnetic field effect may result.

First, one can discuss our systems with respect to the hfi mechanism. The initial state of the radical pairs is triplet.[22] Because the rate of S–T_+ and S–T_- crossing is decreased by the magnetic field, the fraction of the triplet pairs is increased, which results in more free radicals and therefore higher cross-linking efficiency. Above a certain field strength, only S–T_0 crossings may occur, and a further increase in field strength does not alter the field effect. This was observed for all systems under investigation.

Second, a Δg mechanism should be considered. The Δg values for our radical pairs are close to 16×10^{-4} for deoxybenzoin and 3×10^{-4} for benzophenone.[23] Our modified SBRs are also ketones, and it can be supposed that their Δg values have the same order of magnitude as the corresponding low molecular ketones. Such Δg values should in principle be sufficient for the appearance of a maximum of the magnetic field effect.[14,15] However, this is not confirmed by our experimental data.

A further result to be explained is the comparatively small magnetic field effect in photocross-linking of the

SBR with phenylacetylphenyl groups compared with the corresponding SBR/deoxybenzoin mixture. The covalent bonding of the photosensitive group to polymer chain has a marked influence on the results. The explanation could lie in the well-known fact that the magnetic field effect depends strongly on the lifetime of the radical pairs.[5] It is obvious that segments of macromolecules in a solvent-free polymer matrix do not always have the same mobility as low molecular molecules in this matrix. Thus, the lifetime should be different for a radical pair consisting of a low molecular and a macroradical compared with a radical pair consisting of two low molecular radicals.

Registry No. $C_6H_5CH_2COC_6H_5$, 451-40-1; $C_6H_5COC_6H_5$, 119-61-9; $C_6H_5CH_2COCH_2C_6H_5$, 102-04-5; $C_6H_5COC_6H_4CH_3$, 134-84-9.

References and Notes

(1) Rabek, J. F. *Mechanisms of Photophysical Processes and Photochemical Reactions in Polymers*; Wiley: Chichester, 1987.
(2) Horie, K.; Ando, H.; Mita, I. *Macromolecules* **1987**, *20*, 54.
(3) Ng, H. C.; Guillet, J. E. *Macromolecules* **1985**, *18*, 2294.
(4) Guillet, J. E. *Polymer Photophysics and Photochemistry*; Cambridge University Press: Cambridge, 1985.
(5) Reviews: Atkins, P. W.; Lambert, T. P. *Annu. Rep. Chem. Soc., Sect. A: Phys. Inorg.* **1975**, *67*. Salikhov, K. M. In *Spin Polarization and Magnetic Effects in Radical Reactions*; Molin, Yu. N., Ed.; Elsevier: Amsterdam, 1984; Chapter 3. Turro, N. J. *Proc. Natl. Acad. Sci. U.S.A.* **1983**, *80*, 609.
(6) Turro, N. J.; Mattay, J. *J. Am. Chem. Soc.* **1981**, *103*, 4200, and subsequent papers.
(7) Tanimoto, Y.; Shimizu, K.; Itoh, M. *J. Am. Chem. Soc.* **1984**, *106*, 7257.
(8) Martl, M. G. Thesis, Technische Universität Graz, 1984.
(9) Morita, H.; Higasayama, I.; Yamaoka, T. *Chem. Lett.* **1986**, 963.
(10) Schaller, R.; Martl, M. G.; Hummel, K. *Eur. Polym. J.* **1987**, *23*, 259.
(11) Hummel, K.; Schaller, R.; Martl, M. G. *Polym. Bull. (Berlin)* **1987**, *17*, 369.
(12) Martl., M. G.; Pongratz, Th.; Hummel, K. *Makromol. Chem., Rapid Commun.* **1983**, *4*, 649.
(13) Martl, M. G.; Schaller, R.; Hummel, K. *Makromol. Chem.* **1985**, *186*, 2615.
(14) Leshina, T. V.; Salikhov, K. M.; Sagdeev, R. Z.; Belyaeva, S. G.; Mariasova, V. I.; Purtov, P. A.; Molin, Yu. N. *Chem. Phys. Lett.* **1980**, *70*, 228.
(15) Turro, N. J.; Chung, C.-J.; Jones, G.; Becker, W. G. *J. Phys. Chem.* **1982**, *86*, 3677.
(16) Kreyszig, E. *Statistische Methoden und ihre Anwendungen*, 7th ed.; Vandenhoeck & Ruprecht: Göttingen, 1979; p 218.
(17) Schaller, R. Thesis, Technische Universität Graz, 1987.
(18) Heine, H. G. *Tetrahedron Lett.* **1972**, *33*, 3411.
(19) Ng, H. C.; Guillet, J. E. *Macromolecules* **1985**, *18*, 2299.
(20) Scaiano, J. C.; Abuin, E. B.; Steward, L. C. *J. Am. Chem. Soc.* **1982**, *104*, 5673.
(21) Sakaguchi, Y.; Nagakura, S.; Hayashi, H. *Chem. Phys. Lett.* **1980**, *72*, 420.
(22) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, CA, 1978.
(23) Berndt, A.; Fischer, H.; Paul, H. *Magnetic Properties of Free Radicals*; Landolt-Börnstein; Springer-Verlag: Berlin, 1977; Group II, Vol. 9, Part b.

On the Double-Melting Behavior of Poly(ether ether ketone)

Youngchul Lee,*,† Roger S. Porter,† and J. S. Lin‡

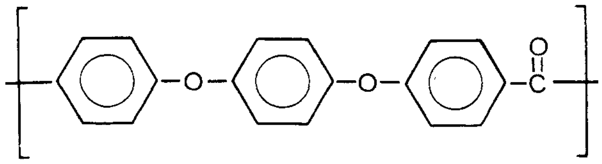
Polymer Science and Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003, and Solid State Division, Oak Ridge National Laboratory,§ Oak Ridge, Tennessee 37831.

Received June 14, 1988;
Revised Manuscript Received September 12, 1988

ABSTRACT: The double-melting behavior of poly(ether ether ketone) (PEEK) has been investigated using differential scanning calorimetry (DSC) and wide- and small-angle X-ray scattering. The peak temperatures of two melting endotherms have been found to depend linearly on the logarithm of the DSC heating rate. At a high heating rate, two endotherms coalesce into a single endotherm which has been considered to represent complete melting without reorganization. The peak temperature of the coalesced endotherm has been found to be approximately the average of the two former peak temperatures at lower heating rates. This behavior has also been observed for poly(ethylene terephthalate) which is known to show two melting endotherms due to crystal reorganization. The average of the two peak temperatures, therefore, has been used in the Thomson–Gibbs equation to estimate the thermodynamic melting point (384 °C) and surface free energy (39 erg/cm^2) of the PEEK crystal. The heat of fusion of the PEEK crystal (39.5 cal/g) has been measured from a linear relationship between the heat of fusion and the density.

Introduction

Poly(ether ether ketone) (PEEK) is a semicrystalline thermoplastic with a glass transition around 145 °C. The chemical structure of PEEK is



Since PEEK shows good mechanical properties, it is currently being studied as a high-performance plastic and as a matrix for fiber-reinforced composites.[1-7]

Differential scanning calorimeter (DSC) traces of PEEK samples which have been isothermally crystallized show two distinct melting endotherms.[8-11] The observation of

---

* Current address: Textile Processing Laboratory, University of Tennessee, Knoxville, TN 37996.

† University of Massachusetts.

‡ Oak Ridge National Laboratory.

§ Operated by Martin Marietta Energy Systems, Inc., for the Division of Materials Sciences, US Department of Energy under Contract DE-AC05-84OR21400.

0024-9297/89/2222-1756$01.50/0 © 1989 American Chemical Society