THE FILE IS NOT THE FINAL PUBLISHED VERSION OF THE PAPER

SEPARATION AND KINETIC ANALYSIS OF THE THERMO-OXIDATIVE REACTIONS OF POLYACRYLONITRILE UPON HEAT TREATMENT

Balázs Szepcsik[1,2,*], Béla Pukánszky[1,2]

[1]Laboratory of Plastics and Rubber Technology, Department of Physical Chemistry and Materials Science, Budapest University of Technology and Economics, H-1521 Budapest, P.O. Box 91, Hungary

[2]Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, H-1519 Budapest, P.O. Box 286, Hungary

*Corresponding author. Tel.: +36203905822; E-mail:
szepcsikb@ch.bme.hu (B. Szepcsik)

Abstract

A polyacrylonitrile (PAN) homopolymer and a copolymer with methyl acrylate (MA) were analyzed by differential scanning calorimetry (DSC) in order to establish a method for the kinetic analysis of the stabilization reaction steps during heat treatment. The application of a program rarely used for the study of the chemical transformation of PAN and its copolymers resulted in five separate steps, which can be assigned with large probability to various cyclization and oxidation reactions. A more exact identification of the reactions need further measurements and considerations. Overlapping peaks appearing in the DSC traces were deconvoluted and then quantitatively analyzed to obtain kinetic parameters. The kinetics of the processes were described by the Kissinger model. The model could be fitted well to four of the five processes indicating that these belong to individual reactions of the first order. The parameters obtained agree well with the few values published in the literature up to now. The results have large practical relevance, since the kinetic parameters obtained can be used in the preparation of intermediates and for the optimization of the stabilization process.

cyclization, DSC, deconvolution, reaction kinetics, Kissinger analysis

1. Introduction

Polyacrylonitrile and related polymers have been studied in different ways for several decades because of their importance as precursors for carbon fiber production. The procedure comprises of thermo-oxidative stabilization reactions, followed by carbonization and graphitization in inert atmosphere. The application of such materials in composites together with carbon nanotubes is also of growing interest.

In carbon fiber production stabilization is necessary before carbonization and it consists of a series of reaction steps which transform the long chain linear polymer into a partially cross-linked, cyclic structure. The mechanism of these exothermic stabilization steps was studied by several groups in the past, but all details have not been clarified yet. Several papers summarizing the results obtained up to now were published in 1991, 2009 and 2012 [1-3].

During the investigation of a complex, multi-step process, researchers can either follow the overall chemical reaction and its characteristics, or study each or some of the individual elementary steps. The two approaches result in different values

3

for the kinetic parameters, which are used for the calculation of reaction rates. The temperature dependence of reaction rate is usually described by the Arrhenius-equation (1)

$$k = A \exp\left(-\frac{E_a}{RT}\right) \qquad (1)$$

where k is the rate constant, A is the Arrhenius pre-exponential factor, E_a is the activation energy (J/mol) of the reaction, T the absolute temperature (K) and R the universal gas constant, 8.314 J/(molK).

E_a and A values have been reported by several authors for the stabilization of PAN [4-29]. Some of them determined overall rate and described these values for a single process [4-16], while others calculated parameters for two individual processes assuming that the two peaks appearing on the DSC trace represent cyclization and oxidation [9,14,17-27]. Only a minority of the papers reporting kinetic values distinguished three separate reaction steps and usually identified them either as cyclization, oxidation and cross-linking [10,28], or as cyclization, dehydrogenation and oxidation [25,29].

The use of such simplified approaches, which do not resolve overlapping reaction steps, leads to the loss of some kinetic information during the analysis. To make practical use of kinetic parameters, e.g. to utilize them for prediction or explanation, the kinetic analysis must be carried out with great care by

4

choosing a suitable evaluation method. One can benefit from the recommendations summarized in [30] by the Kinetics Committee of the International Confederation for Thermal Analysis and Calorimetry (ICTAC) for this purpose. This guide offers great help to understand the differences among various kinetic methods and their suitability for a given purpose.

A widely used integral isoconversional approach, called the Ozawa-Flynn-Wall method [31] (or Ozawa method [32]), is simply not recommended because of its rough approximation and inaccuracy in the calculation of E_a [30]. Values derived by this approach and reported for the stabilization kinetics of PAN and related copolymers are therefore inaccurate [9-12,14, 16,19,24,28].

The other frequently applied procedure for the calculation of E_a and A is the method proposed by Kissinger [33]. Despite its popularity, it has some limitations as well that must be taken into consideration during its application [30]. Strictly speaking, Kissinger plots for other than first order reactions are biased by a systematic error. On the other hand, in the case of reactions described by the nth-order or Avrami-Erofeev models, the error made is negligible. The second important limitation of the Kissinger method is that the E_a values obtained can adequately describe only single-step processes. This results

in serious error during the application of the Kissinger method for multiple, overlapping reactions steps not separated from each other, and biases numerous results reported in the literature [4,7-10,14-17,26-29]. In a review of the Kissinger equation [34], Baine and Kissinger himself gave some practical recommendations for the proper application of the method for kinetic analysis. We applied these technical suggestions during the execution and evaluation of our DSC measurements.

The aim of the present work was to establish a way of studying the stabilization reactions of acrylonitrile polymers that provides reliable kinetic information and enables the better understanding of the mechanism of the process. Instead of carrying out DSC runs either only in air or nitrogen and then performing a kinetic analysis on the overall trace recorded, we decided to separate the reaction steps and analyze them individually. We studied two of the simplest representatives of these materials, a PAN homopolymer and the copolymer of acrylonitrile and methyl acrylate. The latter could have been investigated as a fiber or as a polymer powder. Since the stabilization of fibers can be controlled by diffusion over chemistry [2], in order to understand the reaction kinetics better and to eliminate the effect of diffusion as much as possible, it seemed to be more rewarding to perform the basic

analysis on polymer powder samples instead.

2. Experimental

2.1 Materials

The two samples analyzed in the present work are commercial materials with the weight average molecular weight (M_w) of 150 kDa. The first is a homopolymer from Sigma-Aldrich Co. (US), while the second is a copolymer from Haihang Industry Co. (China) with 5.5 mol% MA content. Both samples were dried under nitrogen gas at room temperature before DSC analysis.

2.2 Characterization

DSC analysis (Q2000, TA Instruments) was carried out in order to separate stabilization reactions taking place during the heat treatment of PAN. Non-isothermal temperature programs were applied, the samples were heated first in nitrogen atmosphere, followed by a second heating cycle in air. The flow rate of the gases was 60 mL/min.

In order to compensate the „tau lag" effect, the instrument was calibrated at each heating rate applied with an indium standard. The negative effect of the „leading edge slope" was corrected by indium calibration as well. Because of the self-heating effect of exothermic reactions, the maximum heat

generation was kept under 8 mW. The sample mass was 1 mg with a tolerance of ± 0.01 mg. To ensure sufficient gas exchange, pans without lids were used (Tzero Aluminum Low-Mass Pan, pan mass varied between 19.5-20.0 mg). Two runs were carried out and averaged for each condition with heating rates of Φ = 0.7, 1, 2, 4, 7, 10 K/min.

The Universal Analysis (TA Instruments) and the OriginPro 8.6 (OriginLab) softwares were used for data analysis and for the deconvolution of overlapping peaks, respectively. All processes cannot be distinguished without deconvolution and in the case of the severe overlap of two peaks, the determination of the peak temperature is significantly biased. The lack of deconvolution of multiple-step DSC peaks leads to inaccurate results from the Kissinger method.

3. Results and Discussion

3.1 DSC analysis and deconvolution

Heating the homopolymer sample in nitrogen according to the method described above resulted in two overlapping peaks which could be easily distinguished, and in three others during the second heating in air. These latter peaks are quite difficult to differentiate and even the fitting of appropriate functions to

the peaks during deconvolution is slightly uncertain. We found the best fit by using a Gaussian function for Processes II-V, and a Lorentzian function in the case of Process I during deconvolution.

Fig. 1 shows a typical DSC trace recorded on the homopolymer. The processes denoted as PI-V are presumably different thermal and thermooxidative reaction steps. Processes I and II are induced thermally, while Processes III-V occur only in oxidative environment following Processes I and II. If Processes I and II are not separated from the oxidative processes by heating the sample in inert atmosphere first, and the sample is investigated in air or oxygen from the beginning, the overlapping of all five processes makes it very difficult to separate or even distinguish them, as Fig. 2 shows. The determination of their kinetic parameters is even more difficult or even impossible. We presume that Processes I and II are related to the formation of cyclic structures, while Processes III-V are different reactions in which oxygen is bonded into the structure.

In the case of the copolymer, Process II did not appear on the DSC trace (Fig. 3). This peak could not be observed even when the sample was heated up to higher temperatures during the first run at faster heating rates. This indicates the formation

of different chemical structures for the homopolymer and the copolymer during heating. Based on the results of DSC measurements these differences cannot be identified, further experiments must be carried out by NMR and FTIR spectroscopy for this purpose.

In order to demonstrate the quality of the peak fitting procedure, in Table 1 we summarize the determination coefficients (R^2) obtained. The values exceed 0.94 for every trace and peak. The quality of the fitting is of high importance, since all kinetic calculations use the fitted curves.

3.2 Kinetic analysis by the Kissinger method

Kinetic calculations were carried out for each process according to the method of Kissinger [33] for both polymer samples. The Kissinger equation (Eq. 2) is used for the determination of E_a and A

$$\ln \frac{\Phi}{T_p^2} = -\frac{E_a}{R}\frac{1}{T_p} + \ln \frac{A\,R}{E_a} \tag{2}$$

where Φ is the heating rate in K/min, T_p is the peak temperature of the process analyzed, while A, E_a and R correspond to the parameters of the Arrhenius equation (see Eq. 1).

After the deconvolution of overlapping peaks, the resulting peak temperature of a certain process was determined from the DSC traces at different heating rates (Φ = 0.7, 1, 2, 4, 7 and

10 K/min). Subsequently, the $\ln(\Phi/T^2_p)$ quantity was plotted against $1/T_p$ and a linear function was fitted to the average values. The intersection of the line gives $\ln(AR/E_a)$, while its slope corresponds to $-E_a/R$. The Kissinger plot obtained for Process I occurring in the homopolymer during heating is shown in Fig. 4.

The large R^2 values obtained during the linear fitting of the Kissinger model to the data justify the use of the approach for the description of the kinetics of chemical processes taking place during the heating of the samples. Before the analysis we decided not to accept linear fits with an R^2 value smaller than 0.75. We set this relatively low limit, because all processes do not necessarily follow first order kinetics, and a small R^2 value may indicate a different reaction order, the use of a wrong function for deconvolution, or an error committed during the DSC run.

The kinetic parameters calculated from the Kissinger analysis for the two samples are summarized in Table 2. In the case of Process I we could fit a straight line with extremely large R^2 value for both the homopolymer and the copolymer. For the third process we did not obtain a linear Kissinger plot for either of the samples, R^2 values were smaller than 0.75 in both cases. The fact that this reaction might not follow first order

kinetics could be a plausible explanation for the small R^2 values. Fast reaction rate in PIII might be another reason for the deviation. After the preliminary steps taking place during heating in nitrogen, oxidative reactions may start as soon as the material contacts oxygen already at lower temperatures, therefore even small deviations in the temperature program used may result in differences in the first oxidation step. This may also affect subsequent oxidation steps, the noticeable overlap of the three processes and possible changes in the initiation of the oxidation reactions may lead to the deviations experienced in the repeated DSC runs. These effects may also explain the small R^2 values obtained during the fitting of the Kissinger model to Processes IV-V.

In the case of the copolymer, the second process was absent, a significant difference which needs further study. The occurrence of a Diels-Alder cycloaddition reaction might offer a tentative explanation for the phenomenon, as suggested by Sivy, Gordon and Coleman [35]. That reaction does not take place during the heat treatment of the copolymer because of its high comonomer content and the smaller probability of the formation of PAN segments with partially eliminated structures of suitable tacticity, as shown in Fig. 5. Other possible reactions occurring during cyclization are summarized and discussed by Bashir [1].

The activation energy of the first and fifth reaction steps were smaller by about 100 kJ/mol for the copolymer, than the same values of the homopolymer. We assume that the large E_a of both the cyclization and the oxidation reactions of the homopolymer is caused by its more regular structure compared to that of the copolymer.

3.3   Comparison of the results to previously reported data

The results of a kinetic analysis were reported by several authors for PAN and for its copolymer with methyl acrylate [7,9-12,14,16-17,19,22,26]. Mostly the unresolved peaks of samples heated in air were analyzed without any deconvolution. A DSC trace measured under such conditions on the copolymer is shown in **Fig. 6**. Some groups carried out a DSC run in nitrogen as well [10,17,19]. In the case of the copolymer, the trace recorded in inert atmosphere is very similar to the one produced by us showing a single peak, which corresponds to Process I. The E_a and ln$A$ values determined by us and published in the literature before [10,17,28] are summarized in Table 3.

Fitzer and Müller reported an E_a of 106.8 ± 2.5 kJ/mol and ln$A$ of 22.4 ± 1.7 in 1975 [17]. These results are almost identical to those determined by us (110.1 kJ/mol and 21.4). The good agreement of these values can be attributed to the very

similar composition of the investigated materials (5.0 and 5.5 mol percent MA content) as well as to the same method applied, including the weight of the samples analyzed (2 mg and 1 mg, respectively).

Y. Liu et al. [10] studied a homopolymer PAN sample with a similar method that we used, first heating the sample in nitrogen and then in air. They found three peaks and identified them as cyclization, oxidation and cross-linking, most probably corresponding to Processes I, IV and V in our nomenclature. However, the kinetic parameters determined are quite different (140.2 vs 210.1 kJ/mol and 98.1 vs 55.1 kJ/mol) for Processes I and IV, which can be explained by the absence of deconvolution in their analysis. On the other hand, the values are practically the same (188.6 vs 185.5 kJ/mol and ln$A$ of 36.3 vs 36.5) for Process V. Since it is the final reaction step of stabilization, it may be affected the least by the overlap with previous processes, which may explain the good agreement of these values.

H.C. Liu et al. [28] also applied similar DSC conditions in their study. Despite the fact that they studied a polymer with different characteristics (it was a copolymer with 4 wt% of methacrylic acid, MAA), the results are comparable because of the similar DSC method applied. The identification of the peaks was the same as in [10], i.e. cyclization, oxidation and cross-

linking. The effect of MAA can be observed on the resulted DSC traces, namely a significantly lower initiation temperature and lower temperature of the cyclization peak. The parameters determined agree well (with this) for Processes I and V, showing smaller E_a and ln$A$ values. However, the relatively large E_a of Process IV may result from applying only fast heating rates for the kinetic analysis (5, 10 and 15 K/min) and from the absence of deconvolution.

4. Conclusions

The application of a heating program rarely used for the study of the chemical transformation of PAN and its copolymers resulted in five separate steps during the heating of the samples. The heating regime used allowed the clear separation of the five processes, which can be assigned with large probability to various cyclization and oxidation reactions. A more exact identification of the reactions need further measurements and considerations. The peaks appearing in the DSC traces were deconvoluted and then quantitatively analyzed to obtain kinetic parameters. The kinetics of the processes were described by the Kissinger model. The model could be fitted well to four of the five processes indicating that these belong to individual reactions of the first order. The parameters obtained agree well

with the few values published in the literature up to now. The results have large practical relevance, since the kinetic parameters obtained can be used in the preparation of intermediates and for the optimization of the stabilization process.

5. Acknowledgements

References

[1]   Z. Bashir, A critical review of the stabilisation of polyacrylonitrile, *Carbon* **29** (8) (1991) 1081-1090.

[2]   X. Huang, Fabrication and properties of carbon fibers, *Materials* **2** (4) (2009) 2369-2403.

[3]   Y. Liu, S. Kumar, Recent progress in fabrication, structure, and properties of carbon fibers, *Polymer Reviews* **52** (3) (2012) 234-258.

[4]   N. Popovska, I. Mladenov, Untersuchungen zur Herstellung von Kohlenstoffasern auf der Basis von mit Wasserstoffperoxid modifizierten PAN-Fasern, *Carbon* **21** (1) (1983) 33-38.

[5]   O.P. Bahl, R.B. Mathur, T.L. Dhami, Modification of polyacrylonitrile fibres to make them suitable for conversion into high performance carbon fibres, *Materials Science and Engineering* **73** (1985) 105-112.

[6]   R.B. Mathur, O.P. Bahl, V.K. Matta, K.C. Nagpal, Modification of PAN precursor – its influence on the reaction kinetics, *Carbon* **26** (3) (1988) 295-301.

[7]   P. Bajaj, T.V. Sreekumar, K. Sen, Thermal behaviour of acrylonitrile copolymers having methacrylic and itaconic acid comonomers, *Polymer* **42** (2001) 1707-1718.

[8]   S. Hajir Bahrami, P. Bajaj, K. Sen, Thermal behaviour of acrylonitrile carboxylic acid copolymers, *Journal of Applied Polymer Science* **88** (3) (2003) 685-698.

[9]   Q. Ouyang, L. Cheng, H. Wang, K. Li, Mechanism and kinetics of the stabilization reactions of itaconic acid-modified polyacrylonitrile, *Polymer Degradation and Stability* **93** (2008) 1415-1421.

[10]   Y. Liu, H.G. Chae, S. Kumar, Gel-spun carbon nanotubes/polyacrylonitrile composite fibers. Part II: Stabilization reaction kinetics and effect of gas environment, *Carbon* **49** (2011) 4477-4486.

[11]   L. Zhang, Y. Dai, Y. Kai, R. Jin, Structural evolution and kinetic study of high isotacticity poly(acrylonitrile)

during isothermal pre-oxidation, *Carbon Letters* **12** (4) (2011) 229-235.

[12]   S. Rwei, T. Way, Y. Hsu, Kinetics of cyclization reaction in poly(acrylonitrile-methyl acrylate-dimethyl itaconate) copolymer determined by a thermal analysis, *Polymer Degradation and Stability* **98** (2013) 2072-2080.

[13]   Y. Xue, J. Liu, J. Liang, Kinetic Study of the Dehydrogenation Reaction in Polyacrylonitrile-Based Carbon Fiber Precursors during Thermal Stabilization, *Journal of Applied Polymer Science* **127** (1) (2013) 237-245.

[14]   A. Ju, M. Luo, K. Zhang, M. Ge, Mechanism and kinetics of stabilization reactions of poly(acrylonitrile-co-3-aminocarbonyl-3-butenoic acid methyl ester), *Journal of Thermal Analysis and Calorimetry* **117** (1) (2014) 205-215.

[15]   H. Khayyam, M. Naebe, O. Zabihi, R. Zamani, S. Atkiss, B. Fox, Dynamic Prediction Models and Optimization of polyacrylonitrile (PAN) Stabilization Processes for Production of Carbon Fiber, *IEEE Transactions on Industrial Informatics* **11** (4) (2015) 887-896.

[16]   Z. Fu, J. Ma, Y. Deng, G. Wu, C. Cao, H. Zhang, Structural evolution of poly(acrylonitrile-codimethyl itaconate) copolymer during thermal oxidative stabilization, *Polymers for Advanced Technologies* **26** (4) (2015) 322-329.

[17] E. Fitzer, D.J. Müller, The influence of oxygen on the chemical reactions during stabilization of PAN as carbon fiber precursor, *Carbon* **13** (1975) 63-69.

[18] Jr. L.H. Peebles, P. Peyser, A.W. Snow, W.C. Peters, On the exotherm of polyacrylonitrile: Pyrolisis of the homopolymer under inert conditions, *Carbon* **28** (5) (1990) 707-715.

[19] J. Kim, Y.C. Kim, W. Ahn, C.Y. Kim, Reaction mechanisms of polyacrylonitrile on thermal treatment, *Polymer Engineering and Science* **33** (22) (1993) 1452-1457.

[20] H. Kakida, K. Tashiro, M. Kobayashi, Mechanism and kinetics of stabilization reaction of polyacrylonitrile and related copolymers I., *Polymer Journal* **28** (1) (1996) 30-34.

[21] H. Kakida, K. Tashiro, M. Kobayashi, Mechanism and kinetics of stabilization reaction of polyacrylonitrile and related copolymers II., *Polymer Journal* **29** (4) (1997) 353-357.

[22] H. Kakida, K. Tashiro, M. Kobayashi, Mechanism and kinetics of stabilization reaction of polyacrylonitrile and related copolymers III., *Polymer Journal* **29** (7) (1997) 557-562.

[23] R. Devasia, C.P. Reghunadhan Nair, P. Sivadasan, B.K.

Katherine, K.N. Ninan, Cyclization reaction in poly(acrylonitrile/itaconic acid) copolymer: An isothermal differential scanning calorimetry kinetic study, *Journal of Applied Polymer Science* **88** (4) (2003) 915-920.

[24] S.S. Belyaev, I.V. Arkhangelsky, I.V. Makarenko, Non-isothermal kinetic analysis of oxidative stabilization processes in PAN fibers, *Thermochimica Acta* **507-508** (2010) 9-14.

[25] Y. Xue, J. Liu, J. Liang, Correlative study of critical reactions in polyacrylonitrile based carbon fiber precursors during thermal-oxidative stabilization, *Polymer Degradation and Stability* **98** (2013) 219-229.

[26] Z. Fu, Y. Gui, S. Liu, Z. Wang, B. Liu, C. Cao, Effects of an itaconic acid comonomer on the structural evolution and thermal behaviors of polyacrylonitrile used for polyacrylonitrile-based carbon fibers, *Journal of Applied Polymer Science* **131** (19) (2014)

[27] H. Zhang, L. Quan, L. Xu, The effects of carbon nanotubes with acid-groups on the structural evolution and cyclization kinetics of poly(acrylonitrile-co-itaconic acid) composite microspheres, *Fibers and Polymers* **16** (2) (2015) 263-270.

[28] H.C. Liu, A. Chien, B.A. Newcomb, A.A.B. Davijani, S. Kumar, Stabilization kinetics of gel spun polyacrylonitrile/lignin blend fiber, *Carbon* **101** (2016) 382-389.

[29] M.G. Dunham, D.D. Edie, Model of stabilization for PAN-based carbon fiber precursor bundles, *Carbon* **30** (3) (1992) 435-450.

[30] S. Vyazovkin, A.K. Burnham, J.M. Criado, L.A. Pérez-Maqueda, C. Popescu, N. Sbirrazzuoli, ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data, *Themochimica Acta* **520** (2011) 1-19.

[31] J.H. Flynn, L.A. Wall, A quick, direct method for the determination of activation energy by thermogravimetric data, *Polymer Letters* **4** (1966) 323-328.

[32] T. Ozawa, A new method for analyzing thermogravimetric data, *Bulletin of the Chemical Society of Japan* **38** (1965) 1881.

[33] H.E. Kissinger, Reaction kinetics in differential thermal analysis, *Analytical Chemistry* **29** (1957) 1702-1706.

[34] R.L. Baine, H.E. Kissinger, Homer Kissinger and the Kissinger equation, *Themochimica Acta* **540** (2012) 1-6.

[35] G.T. Sivy, B. Gordon, M.M. Coleman, Studies of the

degradation of copolymers of acrylonitrile and acrylamide in air at 200 °C. Speculations on the role of the preoxidation step in carbon fiber formation, *Carbon* **21** (1983) 573-578.

Table 1 Determination coefficients (R^2) obtained during the fitting of various functions to peaks appearing on the DSC traces of PAN polymers

Polymer	Process	Function	Determination coefficient	
			Range	Average
Homopolymer	PI-II	Lorentz	0.953-0.994	0.977
	PIII-V	Gauss	0.950-0.999	0.987
Copolymer	PI	Lorentz	0.945-0.992	0.987
	PIII-V	Gauss	0.943-0.986	0.967

Table 2   Kinetic parameters obtained by the fitting of the Kissinger model to the DSC peaks after deconvolution

Polymer	Process	R^2	E_a (kJ/mol)	$\ln A$
Homopolymer	I	0.994	210.1	44.4
	II	0.955	77.9	13.2
	III	<0.750	–	–
	IV	0.794	55.1	11.7
	V	0.752	185.5	36.5
Copolymer	I	0.998	110.1	21.4
	II	–	–	–
	III	<0.750	–	–
	IV	0.826	45.7	8.6
	V	0.947	83.1	14.4

Table 3 Comparison of kinetic parameters (E_a, A) determined with the help of the Kissinger model to similar values published in the literature

Polymer	Process	E_a (kJ/mol)	ln$A$	Ref.
Homopolymer	I	210.1	44.4	this work
	I	140.2	28.4	10
	I	183.1	38.7	28
	IV	55.1	11.7	this work
	IV	98.1	23.6	10
	IV	87.7	20.6	28
	V	185.5	36.5	this work
	V	188.6	36.3	10
	V	127.0	26.3	28
Copolymer	I	110.0	21.4	this work
	I	106.8	22.4	17
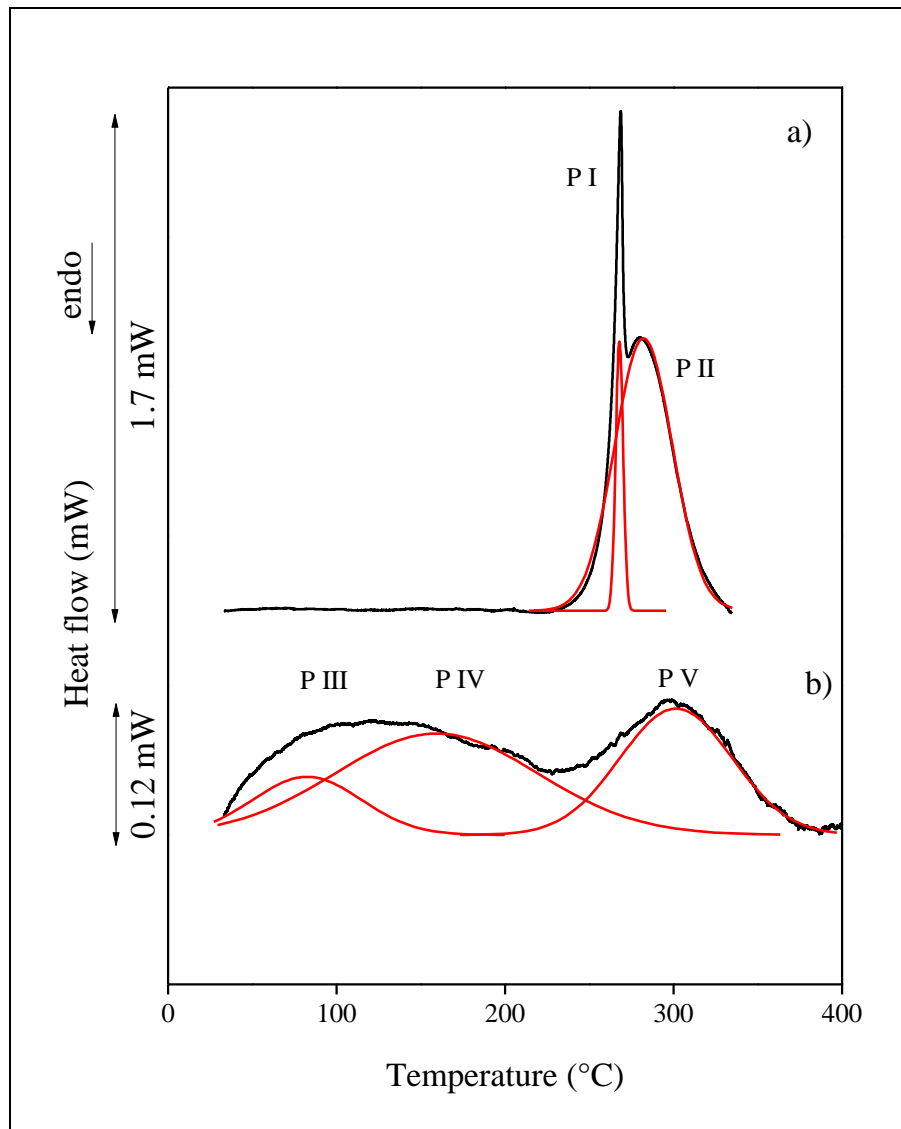
Fig. 1 DSC traces recorded on the PAN homopolymer during heating with the deconvolution of the peaks a) in nitrogen, b) second heating of the sample in air. Φ = 1 K/min.
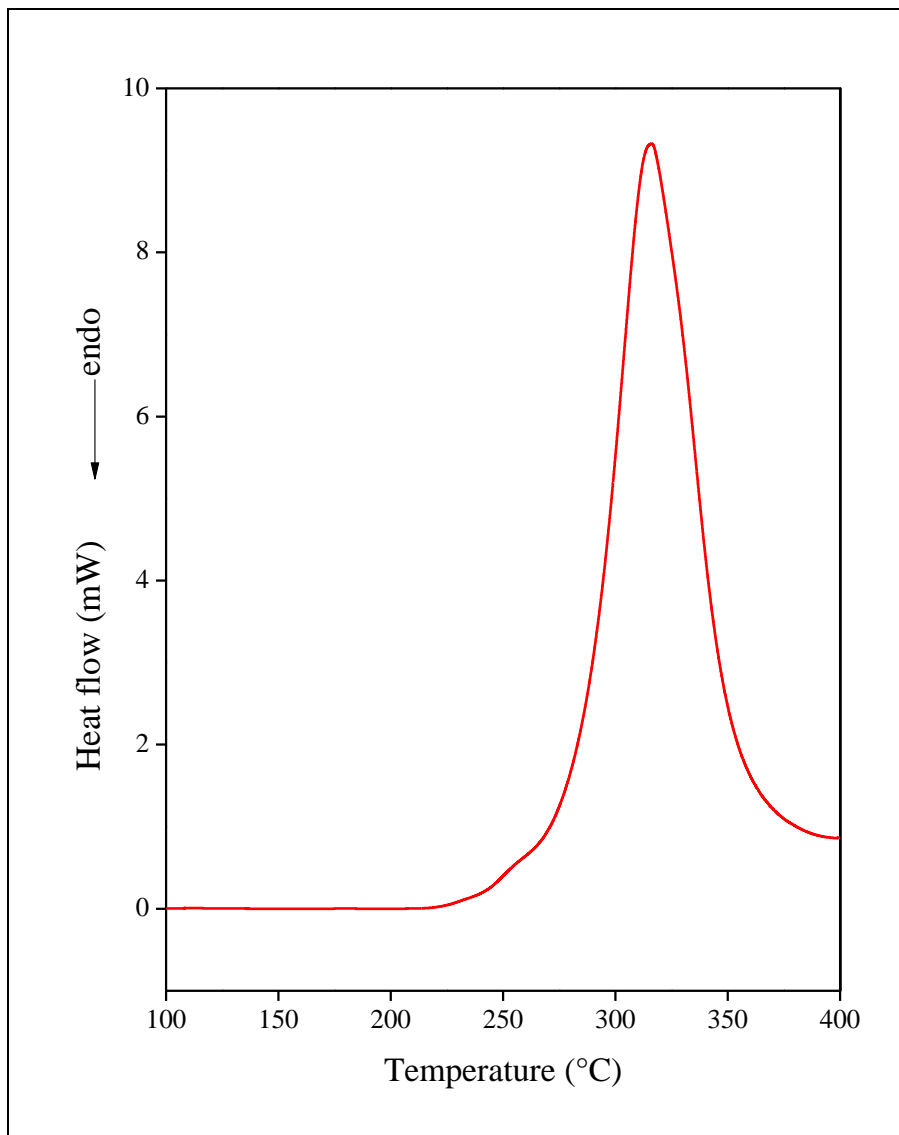
Fig. 2 A DSC trace recorded on the PAN homopolymer in a single step in air, Φ = 5 K/min.
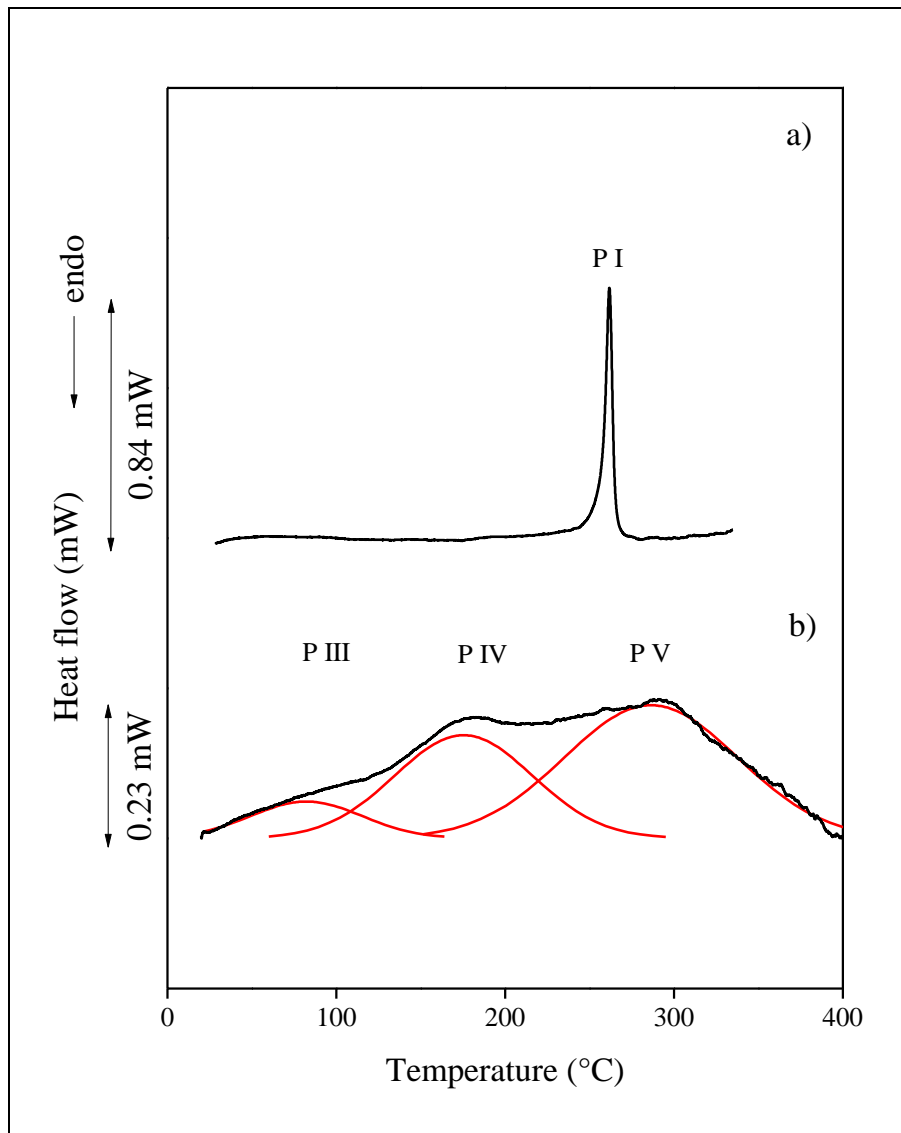
Fig. 3 DSC traces of the poly(acrylonitrile-*co*-methyl acrylate) copolymer with the deconvolution of the peaks. a) in nitrogen b) second heating of the sample in air. $\Phi = 0.7$ K/min.
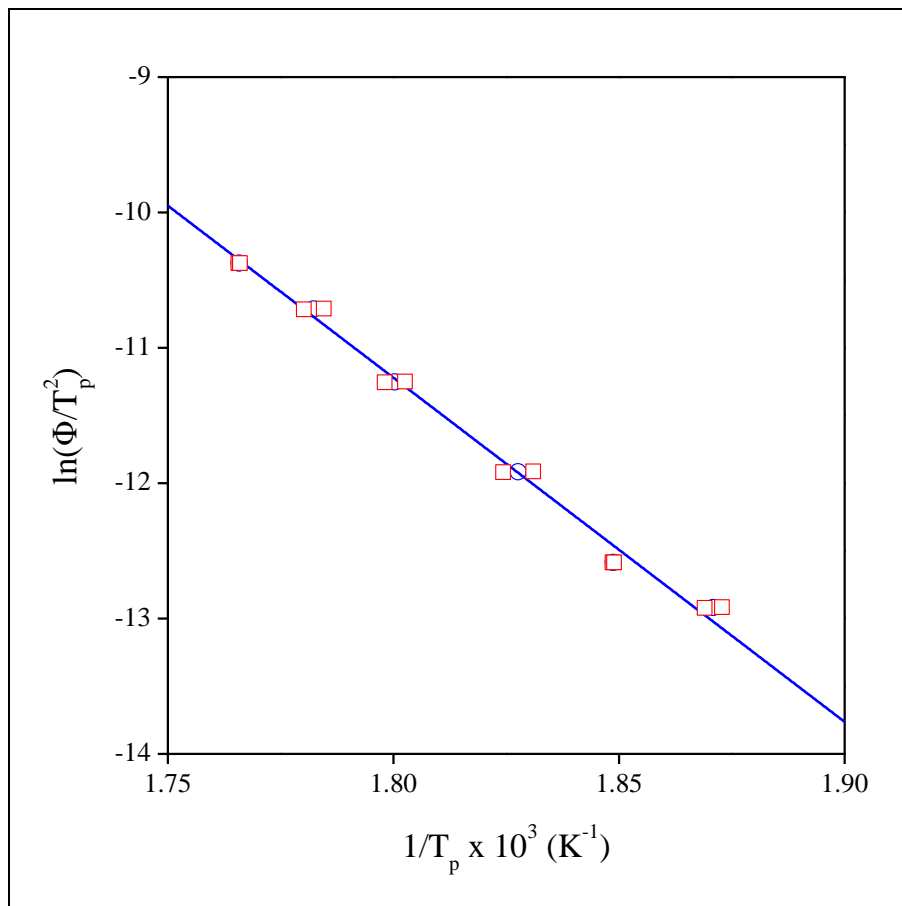
Fig. 4 Kissinger plot of Process I for the PAN homopolymer. Symbols: (□) calculated for each peak temperature separately, (○) average of repeated runs. (——) linear correlation fitted to average values.
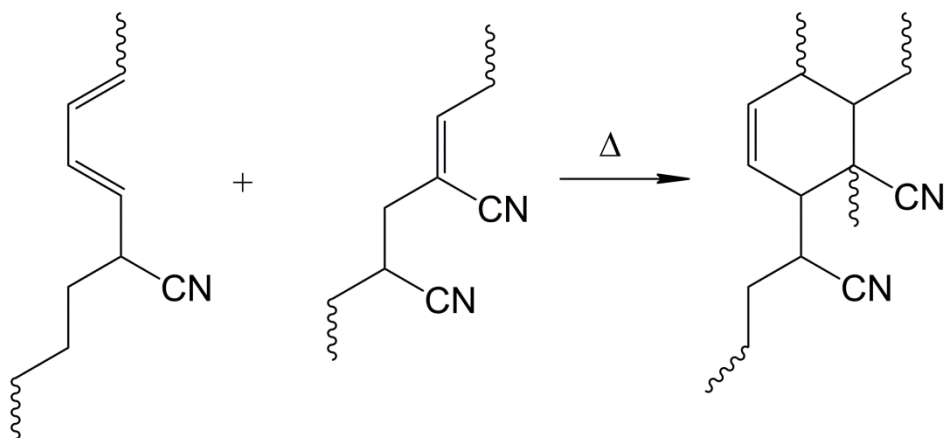
Fig. 5 Diels–Alder reaction of PAN segments with partial elimination as suggested by Sivy, Gordon and Coleman [35]
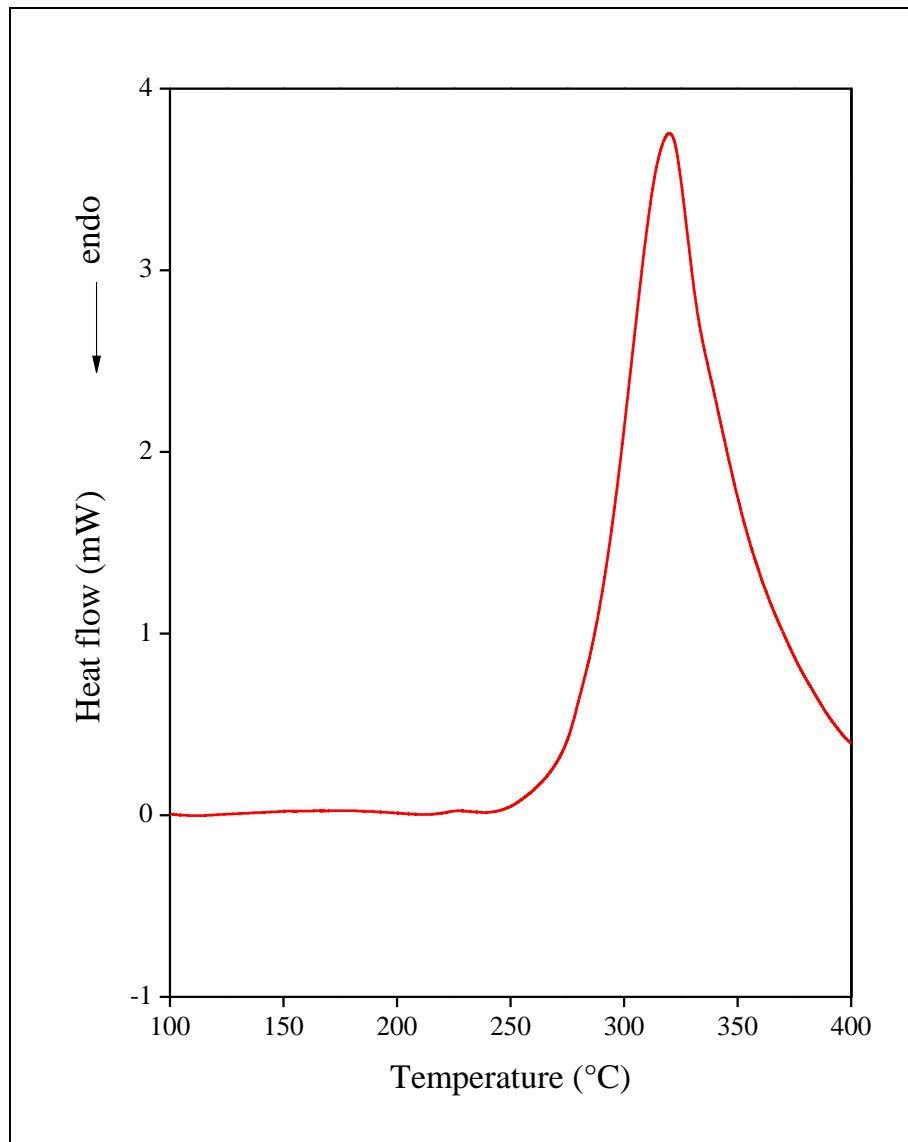
Fig. 6 DSC trace of the poly(acrylonitrile-*co*-methyl acrylate) sample recorded in air, Φ = 5 K/min.