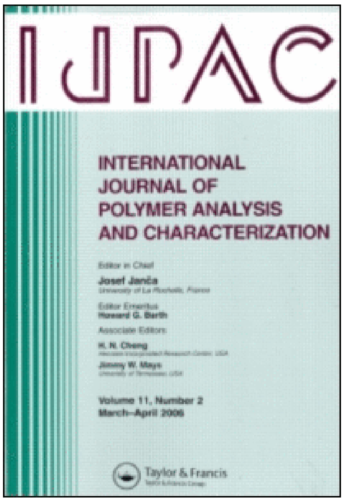


International Journal of Polymer Analysis and Characterization
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646643

Investigation of the Thermal Degradation of Poly(*p*-Nitrostyrene) by Pyrolysis GC-MS

V. V. Zuev[a]; P. V. Zgonnik[a]; L. D. Turkova[a]; L. A. Shibaev[a]
[a] Institute of Macromolecular Compounds of the Russian Academy of Sciences, Sankt-Petersburg, Russian Federation

To cite this Article Zuev, V. V. , Zgonnik, P. V. , Turkova, L. D. and Shibaev, L. A.(2000) 'Investigation of the Thermal Degradation of Poly(*p*-Nitrostyrene) by Pyrolysis GC-MS', International Journal of Polymer Analysis and Characterization, 5: 4, 331 — 337

To link to this Article: DOI: 10.1080/10236660008034631

URL: http://dx.doi.org/10.1080/10236660008034631

Int. J. Polym. Anal. Charact.,
2000 Vol. 5, pp. 331–337
Reprints available directly from the publisher
Photocopying permitted by license only

Investigation of the Thermal Degradation of Poly(*p*-Nitrostyrene) by Pyrolysis GC-MS*

V.V. ZUEV[†], P.V. ZGONNIK, L.D. TURKOVA and L.A. SHIBAEV

Institute of Macromolecular Compounds of the Russian Academy of Sciences, Bolshoi pr.31, Sankt-Petersburg, 199004, Russian Federation

(Received 15 July 1998; In final form 1 February 1999)

The thermal degradation of poly(*p*-nitrostyrene) has been studied by mass spectrometric thermal analysis and pyrolysis gas chromatography. It was shown that the main thermal degradation process is depolymerization. Polymer cross-linking leads to a change in the thermal degradation mechanism.

Keywords: Poly(*p*-nitrostyrene); Thermal degradation mechanism; Mass spectrometric thermal analysis; Pyrolysis gas chromatography

INTRODUCTION

The thermal behavior of nitro compounds has received considerable attention, mainly because of the explosive properties exhibited by these compounds. However, the thermochemistry of low-molecular-weight nitro compounds has been studied in great detail and many reviews have been published,[1–3] whereas the area of polymeric nitro compounds has almost been neglected. The aim of this work was to study the thermal behavior of poly(4-nitrostyrene) (PNS) in the temperature range from 200°C to 600°C.

---

* Presented at the 11th International Symposium on Polymer Analysis and Characterization (ISPAC-11), Santa Margerita Ligure, Italy, May 25–27, 1998.

[†] Corresponding author.

EXPERIMENTAL

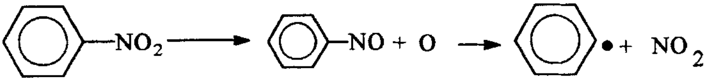
The synthesis of 4-nitrostyrene and PNS are described elsewhere.[4] Mass spectrometric thermal analysis was carried out on an Mkh 1320 instrument (USSR) at 18 eV by the procedure described in Ref. [5] at a heating rate of 6 K/min. A sample with a mass of 0.1 mg was fixed directly onto the thermocouple with the aid of aluminum foil. The thermocouple was introduced through a Teflon® tube directly into the destructor, which greatly increased the precision of the temperature measurements.

Thermogravimetric analysis was performed using a "Derivatograph C" instrument (F. Paulik, J. Paulik and L. Erdey, Hungary). In each case 50 mg of the sample was heated at a heating rate of 10°C/min from ambient temperature to 750°C on air.

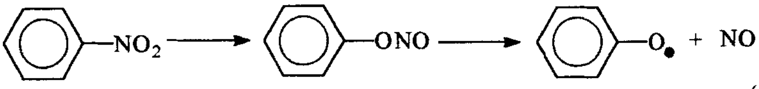
Pyrolysis gas chromatography was carried out on a Tswett 100 chromatograph (USSR) equipped with a pyrolytic flow cell supplied with a magnetic pipette described previously.[6] Gas chromatography analyses were performed using a flame ionization detector and a 1-m×3-mm i.d. stainless-steel column with containing, 30% SE-30 on Chromosorb G. The carrier gas was helium at a flow rate 30 mL/min. Quantitative determination of degradation products was carried out both under isotermic conditions and with column temperature programming in the range of 20–170°C according to direct instrument calibration with mixtures of the corresponding products.

RESULTS AND DISCUSSION

The pyrolysis of aromatic nitro compounds leads to the generation of aromatic free radicals.[1–3] A peculiar feature of polymeric nitro compounds is the fact that these primary free radicals can initiate depolymerization and, as a result, can change essentially the ratio of the degradation products towards the monomer. In fact mass spectrometric thermal analysis shows (see Figure 1 and Table I) that the main products of thermal degradation in the initial stages are the monomer and protonation products under mass spectroscopic conditions. Of the two possible reactions of primary free radical formation from nitro compounds,[7] reaction (1) predominates:



(1)



(2)

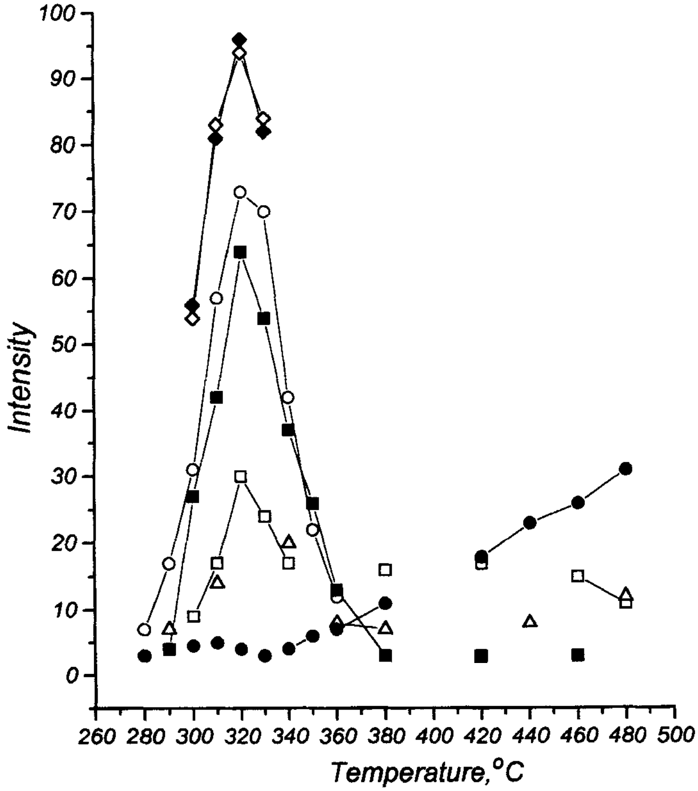
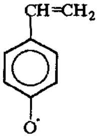
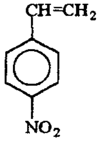
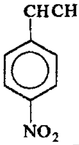
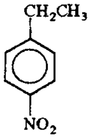
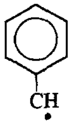


FIGURE 1 Dynamics of the intensity change for the main ions formed during mass spectroscopic thermal analysis of poly(p-nitrostyrene). See Table I for symbol designations.

TABLE I Ions formed during thermal degradation of poly(*p*-nitrostyrene) and detected by mass spectrometric thermal analysis

Structure							
Mass	77	93	119	149	150	151	91
Symbols in Figure 1	●	■	△	◆	◇	○	□

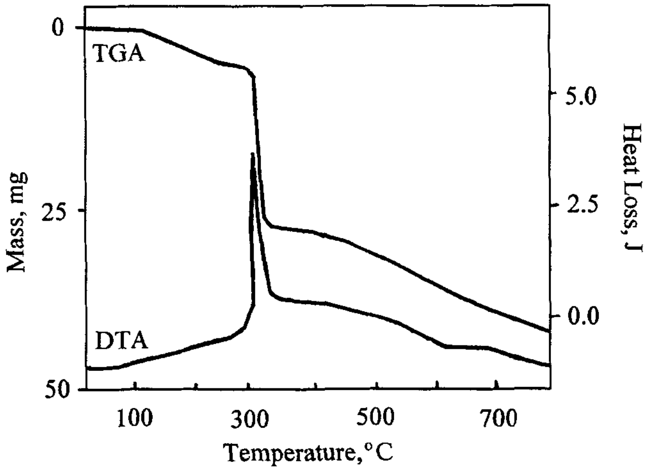


FIGURE 2 DTA and TGA curves for poly(*p*-nitrostyrene).

According to mass spectrometric thermal analysis, the maximum temperature yielding degradation products is 316°C, which is in good agreement with the DTA value of 315°C (Figure 2). According to TGA data, at 335°C about 45% of the residue remains. This residue was assumed to be cross-linked polymer because of its insolubility.

It is well known that the thermal degradation mechanism for linear and cross-linked polymers can differ greatly.[8] This is observed in the present case and can be seen, in particular, for the change in the slope of the DTA and TG curves (Figure 2). According to mass spectrometric thermal analysis (Figure 1), reaction (2) predominates as the primary reaction of free radical generation. Hence, the change in the initiation mechanism of thermal degradation actually takes place.

TABLE II Mass percentage of compounds produced in thermal degradation of 4-nitrostyrene and poly(*p*-nitrostyrene) at various temperatures and conditions of pyrolysis detected by pyrolysis gas chromatography

Compound	*4-nitrostyrene* 200°C	*Poly-(p-nitrostyrene)* 200°C	*Poly-(p-nitrostyrene)* 500°C	*Cross-linked poly(p-nitrostyrene)*[a] 400°C
Aliphatic and nitric hydrocarbons	35	52.0	2.0	25[b]
Benzene	1.0	14.4	0.02	
Toluene	4.0	1.0	0.17	
Styrene	8.0	—	0.2	+
Phenol	1.3	—	<0.2	65.0
Aniline	+	—	<0.2	+
Nitrobenzene	8.0	—	0.1	+
Nitrotoluene	6.0	7.8	0.08	1.1
Biphenyl	1.0	—	0.17	—
Monomer	30	15.0	95.0	8.1
Diphenyloxide	3.0	0.62	+	+
α-methylstyrene	—	0.3	+	+

+ trace.

[a] Produced by heating 500°C during 10 min in a sealed tube.

[b] Aliphatic and nitric hydrocarbons, benzene, toluene.

Comparison of mass spectrometric thermal analysis and pyrolysis gas chromatography results shows that different product compositions of poly(*p*-nitrostyrene) thermal degradation were formed. This difference occurs because the mass spectroscopic method uses thermal, as well as electron ionization. The analysis of the product composition shows that the major trend of poly(*p*-nitrostyrene) thermal degradation is depolymerization (Table II). On the whole the values of the composition of poly(*p*-nitrostyrene) thermal degradation products determined by these methods are in good agreement (Table II). The set of minor products was formed by secondary reactions of phenyl and phenoxide free radicals and is in good agreement with the corresponding products formed during nitrobenzene pyrolysis.[3] Monomer degradation can provide a certain contribution to the set of minor products (Table II). However, this contribution is not essential because at 400–500°C the monomer yield was 90–95% (Figure 3). The pyrolysis gas chromatography analysis of cross-linked poly(*p*-nitrostyrene) also confirms the change in the process mechanism (Table II) being in agreement with the mass spectrometric thermal analysis data.

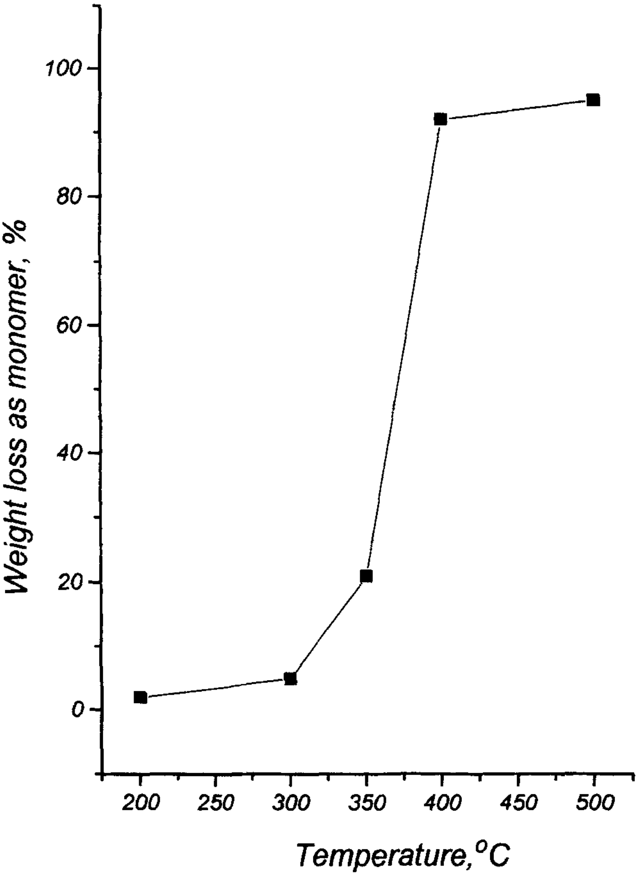


FIGURE 3 Amount of monomer formed during the pyrolysis of poly(*p*-nitrostyrene) detected by pyrolysis gas chromatography as a function of pyrolysis temperature.

Consequently, the insertion of nitro substituents into polystyrene does not lead to a change in the thermal degradation trend, and the predominant process, just as in the case of polystyrene, remains depolymerization.

CONCLUSION

The main products of thermal degradation of poly(*p*-nitrostyrene) in the initial stages is the monomer. At 400–500°C, the monomer yield is

90–95%. Of the two possible reactions of primary free radicals formation from nitro compounds, reaction (1) predominates. Cross-linking leads to a change in the thermal degradation mechanism. For cross-linked polymer, reaction (2) predominates as the primary reaction of free radical generation. The insertion of nitro substituents into polystyrene leads to decreased thermal stability (T_{max} for poly(*p*-nitrostyrene) is 315°C, for polystyrene is 388°C at a heating rate 6 K/min).

References

[1] R.J. Coombs (1979). In: *Comprehensive Organic Chemistry*; D. Barton and W.D. Ollis (Eds.); Vol. 2 . *Nitrogen Compounds*; I.O. Sutherland (Ed.); (Pergamon Press, Oxford), pp. 412–538.

[2] L. Batt (1982). In: *Chemistry of Amino, Nitroso and Nitro Compounds and Their Derivatives*, S. Patai (Ed.); (J. Wiley & Sons, Chichester), pp. 419–513.

[3] E.K. Fields and S. Meyerson (1975). In: *Advances in Free-radical Chemistry*, G.H. Williams (Ed.); (Elek Science, London), pp. 101–145.

[4] M.M. Koton, Yu.V. Mitin and F.S. Florinsky (1955). *Zh. Obsch. Khim.*, **25**, 1469.

[5] L.A. Shibaev, Yu.N. Sazanov, N.G. Stepanov, T.M. Bulina and T.I. Ghukova (1982). *Vysokomol. Soedin. Ser. A*, **24**, 2543.

[6] L.D. Turkova, B.G. Belenkii and E.M. Novikova (1970). In: *Synthesis, Structure and Properties of Polymers*, M.M. Koton (Ed.); (Nauka, Leningrad), pp. 80–85.

[7] C.W. Hand, C. Merrit Jr. and C.D. Di Pietro (1977). *J. Org. Chem.*, **42**, 841.

[8] V.V. Zuev, L.A. Shibaev, N.G. Stepanov, N.A. Solovskaja and A.V. Buriko (1990). *Vysokomol. Soedin. Ser. A*, **32**, 1866.