

Notes

Some Observations on the Thermal Stabilities of Modified N-Vinylcarbazole Polymer Systems

Recent work by Biswas and co-workers¹⁻³ described the novel syntheses of modified *N*-vinylcarbazole (NVC) polymer systems using two different procedures, viz. condensation of NVC with aldehydes and anhydrides and through cationic copolymerization with divinylbenzene (DVB), both in presence of anhydrous AlCl_3 . Thermal stability studies of these products reveal certain interesting features which are highlighted in the present communication.

EXPERIMENTAL

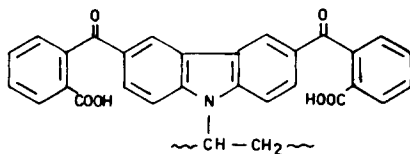
NVC—phthalic anhydride polymer (NVCPA) was prepared by reacting NVC and phthalic anhydride in presence of anhydrous AlCl_3 in benzene medium, following the procedure of Biswas and Packirisamy.²

Poly(*N*-vinylcarbazole) (PNVC) was prepared by carrying out the polymerization of NVC in chlorobenzene medium using AlCl_3 as a catalyst.⁴

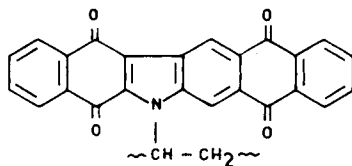
Thermal characteristics of PNVC and NVCPA were studied with a MOM derivatograph over temperatures up to 1000°C in air. The heating rate was maintained at 10°C/min.

RESULTS AND DISCUSSION

Table I compares the thermal stabilities of PNVC, NVCPA, NVC—furfural copolycondensate (NVCF),⁵ and NVC—divinylbenzene copolymer (NVCDVB).⁶ It is seen that the initial stability of PNVC is higher than that of NVCPA. From the TG curves of NVCPA and PNVC, T_0 (the temperature up to which the basic structure of a polymer is retained⁷) of NVCPA (~240°C) is observed to be less than that of PNVC (~400°C). Biswas and Packirisamy² suggested that the reaction of NVC and phthalic anhydride leads to the formation of a keto acid (Scheme I), apparently through



Scheme I.



Scheme II.

the condensation of phthalic anhydride and PNVC formed in the reaction medium. Compared to PNVC, NVCPA (Scheme I) possesses a less compact uncyclized structure from which phthalic anhydride entities may be knocked off well before 400°C (T_0 of PNVC). However, it is interesting to note that from 500°C onwards PNVC undergoes more weight loss than NVCPA. Thus, NVCPA undergoes 76.3% weight loss at 600°C, where PNVC degrades almost completely. This may be probably due to some of the carboxylic acid groups in NVCPA getting cyclized with carbazole moieties to form the quinone (II), at higher temperatures,⁸ thereby resulting in enhanced thermal stability.

TABLE I
Thermal Stabilities of PNVC, NVCPA, NVCF, and NVCDVB

Temperature (°C)	Weight loss ^a (%)			
	PNVC	NVCPA	NVCF	NVCDVB
200	5.0	6.8	no loss	no loss
300	6.0	27.1	no loss	no loss
400	8.0	53.1	22.5	2.0
500	75.0	69.9	39.0	21.0
600	95.0	76.3	58.0	35.0
700	completely degraded	83.8	81.0	55.0
800		89.1	92.5	74.0

^a Calculated from the TG curves of PNVC, NVCPA, NVCF,⁵ and NVCDVB.⁶

In the case of NVCF also the T_0 (~300°C) is less than that for PNVC, while above this temperature NVCF is thermally more stable than PNVC, which is attributed to the presence of some low molecular weight—less crosslinked products in NVCF matrix.⁵

From Table I, it is seen that the thermal stabilities of NVCPA, NVCF, and NVCDVB lie in the order



In NVCPA apparently, interchain crosslinking possibilities are less, whereas NVCF and NVCDVB are reported^{1,3,5,6} to be crosslinked polymeric matrices. Accordingly, it is to be expected that NVCPA should be thermally less stable than the other two. Among NVCF and NVCDVB, NVCF is thermally less stable than NVCDVB which is understood from the fact that NVCF is predominantly a condensation copolymer,¹ whereas NVCDVB is predominantly an addition copolymer.^{3,6} It has been reported^{9,10} that copolymers obtained by condensation copolymerization are generally thermally less stable than those obtained by addition copolymerization. Accordingly, NVCDVB should be expected to be thermally more stable than NVCF.

Cyclization¹¹ of aromatic keto acids may be brought by treatment with concentrated H_2SO_4 . Accordingly, the treatment of NVCPA with concentrated H_2SO_4 would be expected to result in the formation of the quinone (Scheme II) in addition to sulfonation of the polymer. This may cause some improvement in the thermal stability of NVCPA. Table II compares the thermal stabilities of sulfonated products of NVCPA,² NVCF,¹² and NVCDVB.¹³ It is seen that sulfonated NVCF (NVCFs) and sulfonated NVCDVB (NVCDVBS) have almost equal thermal stabilities. However, NVCPAS is thermally more stable than NVCFs and NVCDVBS. It is remarkable that NVCPAS undergoes only 60% weight loss at 800°C, where NVCFs and NVCDVBS degrade to about 90.5% and 95.0% respectively. It is also seen that the overall thermal stability of NVCPA has been improved remarkably by sulfonation which is attributed to the formation of the quinone (II)² during the sulfonation of NVCPA. This quinone will have a closed structure as compared to NVCPA (I), which explains the higher thermal stability of NVCPAS.

In conclusion, addition copolymerization of NVC with divinylbenzene produces polymers of greater

TABLE II
Thermal Stabilities of NVCPAS, NVCFs, and NVCDVBS

Temp (°C)	Weight loss ^a (%)		
	NVCPAS	NVCFs	NVCDVBS
200	13.5	36.2	34.8
300	31.5	50.0	50.0
400	38.5	59.0	56.5
500	44.5	66.2	68.8
600	50.0	74.8	83.0
700	55.0	81.5	93.8
800	60.0	90.5	95.0

^a Calculated from the TG curves of NVCPAS,² NVCFs,¹² and NVCDVBS.¹³

thermal stability than those obtained from the condensation of phthalic anhydride or furfural with NVC. However, sulfonation enhances the thermal stability of NVCPA, but reduces the same in the case of NVCF and NVCDVB.

References

1. M. Biswas and S. Packirisamy, *J. Appl. Polym. Sci.*, to appear.
2. M. Biswas and S. Packirisamy, *J. Appl. Polym. Sci.*, **25**, 511 (1980).
3. M. Biswas and G. C. Mishra, *Makromol. Chem.*, **182**, 261 (1980).
4. M. Biswas and P. Kamannarayana, *J. Polym. Sci., Polym. Chem. Ed.*, **14**, 2071 (1976).
5. M. Biswas and S. Packirisamy, *J. Appl. Polym. Sci.*, in press.
6. G. C. Mishra, Ph.D. thesis, Indian Institute of Technology, Kharagpur, India, 1981.
7. N. D. Ghatge and G. D. Khune, *Angew. Makromol. Chem.*, **79**, 93 (1979).
8. D. K. Saltybaev, S. S. Kozhabekov, Z. A. Shishkina, V. G. Gutsalyuk, and B. A. Zhubanov, *Vysokomol. Soedin. Ser. B*, **16**(10), 776 (1974).
9. N. D. Talanov and G. V. Astakhova, *J. Appl. Chem., USSR*, **39**, 1791 (1966).
10. R. Ramaswamy and N. Krishnaswamy, *Ind. J. Tech.*, **10**, 185 (1972).
11. W. C. Sumpter and F. M. Miller, *The Chemistry of Heterocyclic Compounds*, Interscience, New York, 1954.
12. M. Biswas and K. J. John, *J. Appl. Polym. Sci.*, **23**, 2327 (1979).
13. M. Biswas and G. C. Mishra, *J. Appl. Polym. Sci.*, **26**, 1719 (1981).

MUKUL BISWAS
S. PACKIRISAMY

Department of Chemistry
Indian Institute of Technology
Kharagpur-721302, India

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