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# CO-CURING STUDIES OF ETHYNYL TERMINATED OLIGOIMIDE AND (METHYL) NADICIMIDE RESINS*

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## Abstract

The paper describes the co-curing studies of ethynyl and ethenyl end-capped imide resins. The effect of composition and chemical structure of ethenyl end-capped resins (nadicimides) on thermal behavior of ethynyl end-capped resins was evaluated using DSC and thermogravimetric analysis. An increase in char yield was observed on co-curing of few resin formulations. A mechanism has been proposed to account for this observation.

**Keywords:** DSC, polymers, resins, TG

## Introduction

Polymer blends based on thermosets and thermoplastics have been investigated extensively in the past to improve thermal stability, mechanical properties and toughness characteristics. Thus blending of an easy-to-process but brittle thermosetting polymer with a tough but difficult to process thermoplastic yields a combination with easy processability and good toughness characteristics [1–7].

Co-curing of two or more thermosets has also received attention in the past [8–14]. *In situ* chain extension of bismaleimide resins with diallyl bisphenol A has been successfully used to develop a two component resin with better impact strength [15, 16]. Co-curing of nadicimide and allyl nadicimide resin has been reported to give formulations with better char yields and thermal characteristics [17, 18].

It would be of interest to investigate the co-curing of an ethynyl end-capped resin i.e. thermid resin with high char yielding phosphorus containing nadicimide and methyl nadicimide resins. In this paper the simultaneous curing

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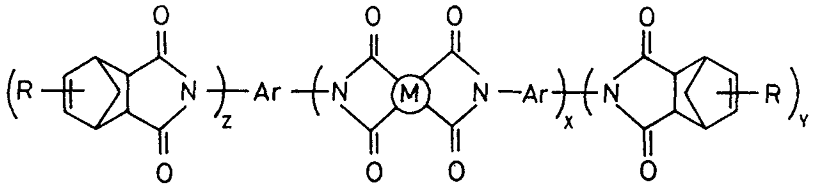
of phosphorus containing (methyl) nadicimide and ethynyl terminated resin is described. Such studies have not been reported in literature.

## Experimental

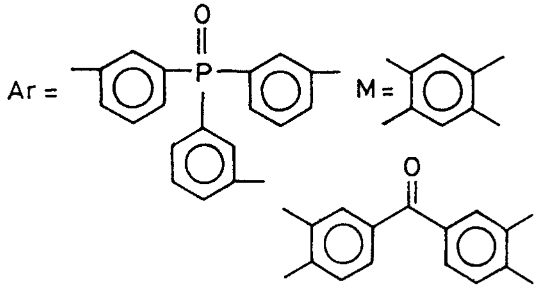
### *Materials*

Ethynyl terminated imide (thermid-600) (designated as *T* in subsequent text) was a commercially available material (National Starch Co., USA) and was used as received.

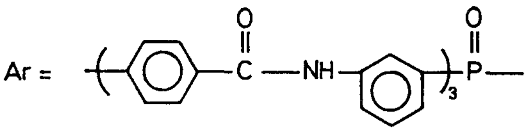
The *bis/tris* nadicimide/methyl nadicimide resins having following structure were synthesised in the laboratories [19–23].



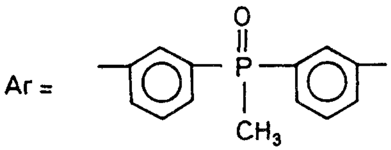
When $R = CH_3$, $X = 1$, $Y = Z = 2$



R = H, X = 0, Y = 2, Z = 1

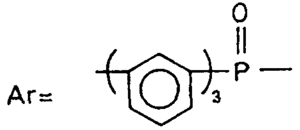


$R = H(CH_3)$, $X = 0$, $Y = Z = 1$



| Resin designation | FMW |
|---|---|
| A | 1464 |
| B | 1572 |
| C | 1118 |
| D<br>(F) | 538<br>(1566) |

$R = CH_3,\ X = 0,\ Y = 2,\ Z = 1$



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## *Sample preparation for co-curing studies*

A homogeneous solution of thermid resin and (methyl) nadicimide resins in a *w/w* ratio of 3:1, 1:1 and 1:3 was prepared in N,N-dimethyl acetamide at room temperature. Solution was stirred for 10 min, and then concentrated un-

**Table 1a** Details of resin formulations for co-curing studies

| Sample | Resins | | | |
|---|---|---|---|---|
| designation | T/g | A/g | B/g | C/g |
| TA$_3$ | 0.1019 | 0.3025 | – | – |
| TA | 0.2003 | 0.2003 | – | – |
| T$_3$A | 0.3001 | 0.1067 | – | – |
| TB$_3$ | 0.1021 | – | 0.3006 | – |
| TB | 0.2028 | – | 0.2018 | – |
| T$_3$B | 0.2988 | – | 0.0968 | – |
| TC$_3$ | 0.1004 | – | – | 0.3000 |
| TC | 0.2011 | – | – | 0.2011 |
| T$_3$C | 0.3000 | – | – | 0.1004 |

**Table 1b** Details of resin formulations for co-curing studies

| Sample | Resins | | | |
|---|---|---|---|---|
| designation | T/g | D/g | E/g | F/g |
| TD$_3$ | 0.1014 | 0.3029 | – | – |
| TD | 0.2018 | 0.2010 | – | – |
| T$_3$D | 0.3250 | 0.1080 | – | – |
| TE$_3$ | 0.0957 | – | 0.3026 | – |
| TE | 0.2000 | – | 0.2010 | – |
| T$_3$E | 0.3033 | – | 0.1080 | – |
| TF$_3$ | 0.1003 | – | – | 0.2993 |
| TF | 0.2000 | – | – | 0.1990 |
| T$_3$F | 0.3056 | – | – | 0.1039 |

der reduced pressure. In order to remove the last traces of solvents, water was added and the precipitated sample was collected and dried in a vacuum oven at 100–150°C for 2 h. The samples have been designated by writing the letter designation of both the resins, with a subscript indicating the ratio of the two constituents taken. For example TA, $TA_3$ and $T_3A$ indicate 1:1, 1:3 and 3:1 (*w/w*) ratio of resin 'T' and 'A' respectively. The details of various resin formulations alongwith their designations are given in Table 1a and 1b.

### *Thermal characterisation techniques*

A DuPont 9900 thermal analyser having a 910 DSC module was used for curing studies of the resins (10±2 mg) in static air at a heating rate of

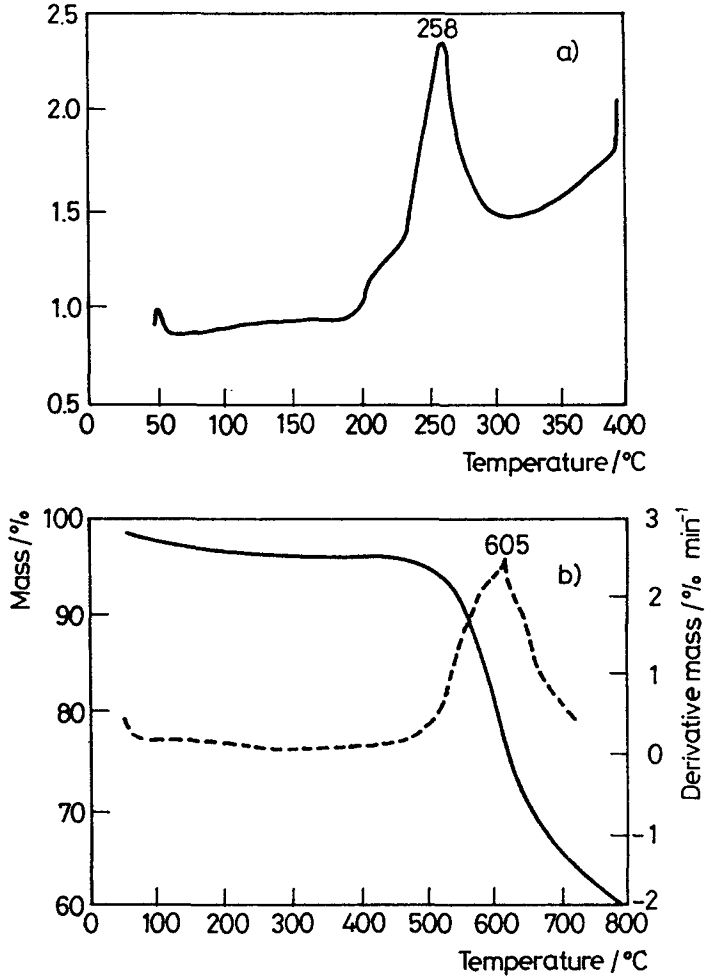


**Fig. 1** DSC scan of resin T (a), TG trace of resin T (b)

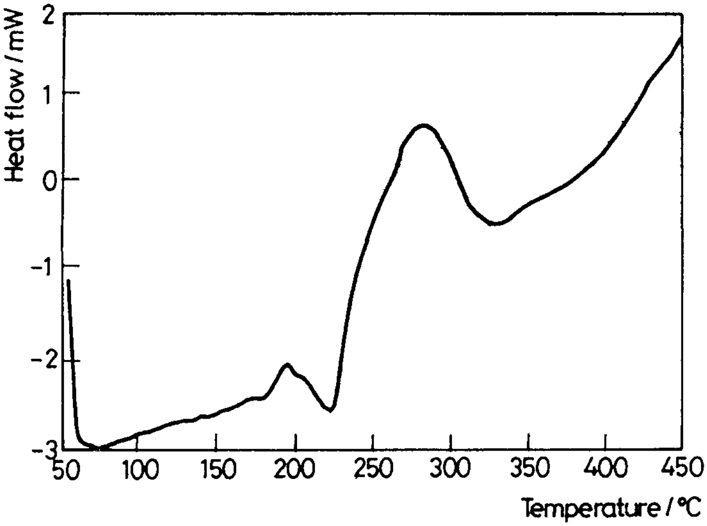


Fig. 2 DSC scan of resin $T_3D$

Table 2 Co-curing studies of ethynyl and ethenyl end-capped imide resins using DSC

| Sl. No. | Sample designation | $T_o$/°C | $T_{exo}$/°C | $T_2$/°C |
|---|---|---|---|---|
| 1. | T | 227 | 258 | 312 |
| 2. | TA | 241 | 276 | 310 |
| 3. | $T_3A$ | 220 | 272 | 312 |
| 4. | $TA_3$ | 286 | 290 | 325 |
| 5. | TB | 240 | 271 | 314 |
| 6. | $T_3B$ | 226 | 268 | 310 |
| 7. | $TB_3$ | 275 | 283 | 310 |
| 8. | TC | 225 | 266 | 320 |
| 9. | $T_3C$ | 230 | 262 | 331 |
| 10. | $TC_3$ | 220 | 246 | 310 |
| 11. | TD | 240 | 283 | 310 |
| 12. | $T_3D$ | – | 280 | 325 |
| 13. | $TD_3$ | – | 280 | 310 |
| 14. | TE | 234 | 283 | 310 |
| 15. | $T_3E$ | 240 | 275 | 310 |
| 16. | TF | – | 275 | 320 |
| 17. | $T_3F$ | – | 280 | 315 |

10°C $\mathrm{min}^{-1}$. The exothermic transition in the DSC trace was characterised by determining $T_o$ – onset temperature of curing and $T_{exo}$ – exothermic peak position (determined by extrapolation).

TG analysis of resins (10±2 mg) was carried out by using DuPont 1090 thermal analyser having a 951 TG module in nitrogen atmosphere (flow rate 60 mL $\mathrm{min}^{-1}$) at a heating rate of 10°C $\mathrm{min}^{-1}$. TG traces were characterised by determining the initial decomposition temperature ($T_i$), the temperature of maximum rate of weight loss ($T_{max}$) and char yield ($Y_c$) at 800°C.

The isothermal curing of (methyl) nadicimide: Thermid-600 was carried out at 325°C for 1 h in a muffle furnace.

## Results and discussion

In resin thermid-600, no endotherm was observed. The curing exotherm was observed in the temperature range of 220–325°C with $T_{max}$ at 258°C (Fig. 1(a)). In TG trace (Fig. 1(b)) the major weight loss was observed between 450–700°C

**Table 3** Mass loss during isothermal co-curing (1h at 325°C) of (methyl) nadicimide and thermid-600 resins

| Sl. No. | Sample designation | Mass loss/% |
|---|---|---|
| 1. | $T_3A$ | 3.59 |
| 2. | TA | 3.14 |
| 3. | $TA_3$ | 1.01 |
| 4. | $T_3B$ | 6.64 |
| 5. | TB | 6.5 |
| 6. | $TB_3$ | 0.38 |
| 7. | $T_3C$ | 10.0 |
| 8. | TC | 9.6 |
| 9. | $TC_3$ | 7.8 |
| 10. | $T_3D$ | 13.7 |
| 11. | TD | 8.7 |
| 12. | $TD_3$ | 13.7 |
| 13. | $T_3E$ | 5.5 |
| 14. | TE | 6.01 |
| 15. | $TE_3$ | 10.2 |
| 16. | $T_3F$ | 15.7 |
| 17. | TF | 1.25 |
| 18. | $TF_3$ | 7.04 |
| 19. | T | 4.10 |

with $T_{max}$ at 612°C (25.6% weight loss). Curing behaviour of nadicimides used in present studies has been reported elsewhere [23].

Co-curing of Thermid with phosphorus containing (methyl) nadicimides, resulted in broadening of curing exotherm in most cases (Fig. 2). On this broad exothermic transition peaks were superimposed in few samples. The onset temperature of curing ($T_o$), exothermic peak position $T_{exo}$ and end of exotherm ($T_2$) obtained from DSC scans are summarised in Table 2.

An increase in methyl nadicimide resins (i.e. A, B, D, E and F) in the resin formulations resulted in an increase in $T_{exo}$ as well as $T_o$ whereas a decrease was

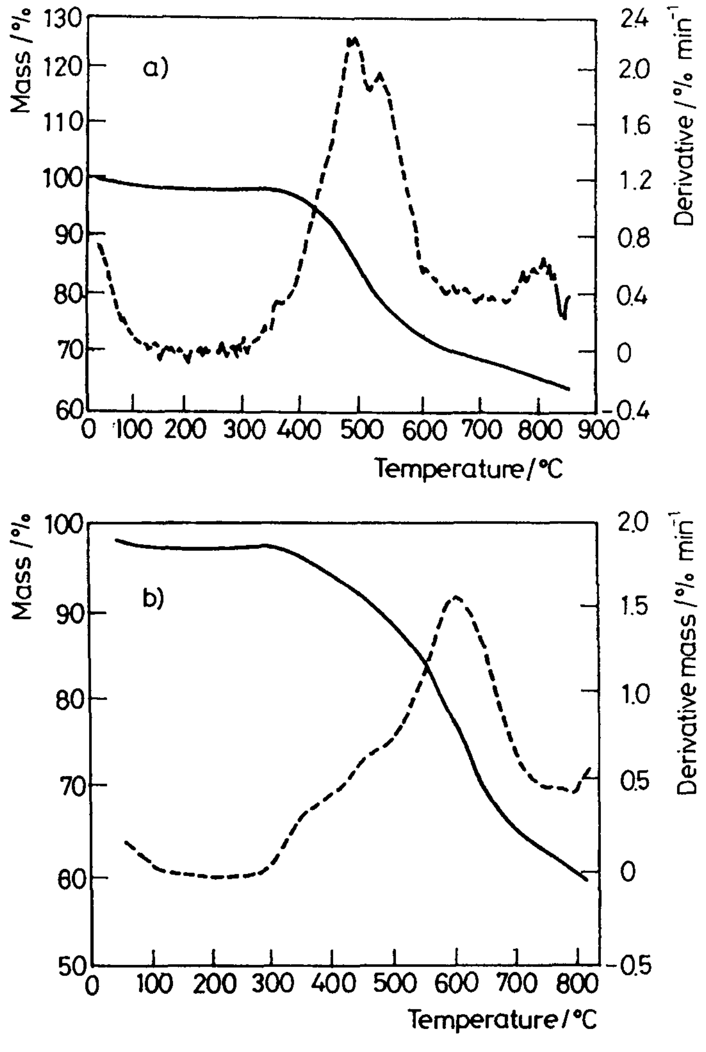


**Fig. 3** TG trace of resins (a) $TE_3$ (b) $T_3E$

observed in case of resin C. Resin C was derived from tris [3-(4-aminobenzamido)phenyl]phosphine oxide (TABP) while other resins were based on tris(3-aminophenyl)phosphine oxide (TAP) and bis(3-aminophenyl)methyl phosphine oxide (BAP).

An endothermic transition between 100–240°C was observed in blends of thermid with resin A and D and in TB, $T_3B$, $TC_3$, $T_3C$.

Isothermal curing of these resin blends was done initially in air atmosphere for 1 h at 275°C. The cured products were found to be partially soluble in DMAc. DSC scans of these co-cured resins showed an exothermic transition indicative of residual curing. Therefore further isothermal curing was done at 325°C for 1 h. Such a treatment resulted in complete curing and no exotherm indicative of residual cure was observed in DSC. Heating at 325°C, resulted in weight loss (Table 3). The weight loss on isothermal curing at 325°C was highest for $T_3F$ (15.7%) and was lowest for $TB_3$ (0.38%)

### *Thermal stability*

TG traces of these co-cured resins are shown in Fig. 3. Initial weight loss of <5% was observed around 100°C but the main degradation started above 400°C.

**Table 4** TG results of co-cured resins containing (methyl) nadicimides and thermid

| Sl. No. | Sample designation | $T_i$/°C | $T_{max}$/°C | $Y_c$/% |
|---|---|---|---|---|
| 1. | $T_3A$ | 475 | 599 | 62.5 |
| 2. | TA | 451 | 598 | 62.5 |
| 3. | $TA_3$ | 447 | 552 | 67.0 |
| 4. | $T_3B$ | 334 | 619 | 60.0 |
| 5. | TB | 402 | 579 | 62.5 |
| 6. | $TB_3$ | 351 | 504 | 69.0 |
| 7. | $T_3C$ | 361 | 503 | 56.5 |
| 8. | TC | 395 | 583 | 61.0 |
| 9. | $TC_3$ | 427 | 612 | 62.0 |
| 10. | $T_3D$ | 453 | 617 | 62.0 |
| 11. | TD | 413 | 525 | 63.0 |
| 12. | $TD_3$ | 302 | 500 | 67.0 |
| 13. | $T_3E$ | 477 | 607 | 60.0 |
| 14. | TE | 398 | 486 | 65.5 |
| 15. | $TE_3$ | 416 | 482 | 66.0 |
| 16. | $T_3F$ | 460 | 625 | 66.0 |
| 17. | TF | 410 | 550 | 65.0 |
| 18. | $TF_3$ | 393 | 470 | 65.0 |
| 19. | T | 540 | 600 | 62.0 |

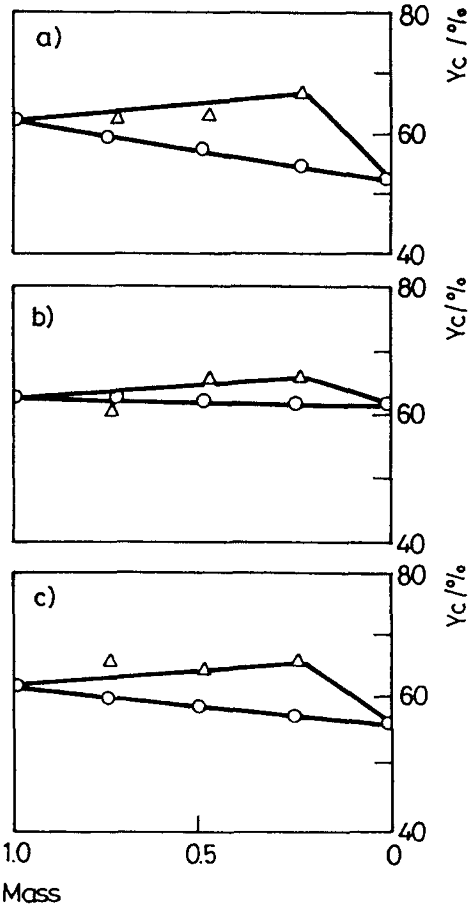


**Fig. 4** Plot of char yield at 800°C *vs.* weight fraction of T in co-cured resins (a) TD (b) TE, (c) TF

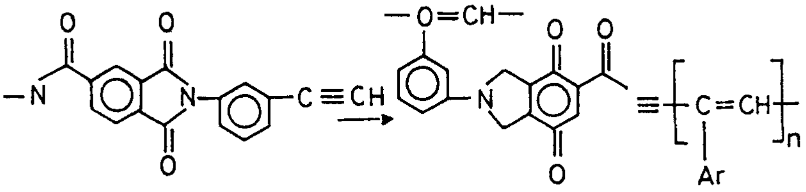
The initial decomposition temperature and temperature of maximum rate of weight loss ($T_{max}$) are given in Table 4.

No systematic trend in $T_i$ and $T_{max}$ values as a function of blend composition was observed.

An increase in (methyl) nadicimides in the resin formulation resulted in an increase in char yield of thermid. The composition having 3:1 ratio of (methyl) nadicimides:thermid resin exhibited char yield higher than neat (methyl) nadicimide resins.

The char yield in co-cured resins were also calculated using the rule of mixtures. The observed char yield in few co-cured samples were higher than the calculated values (Fig. 4).

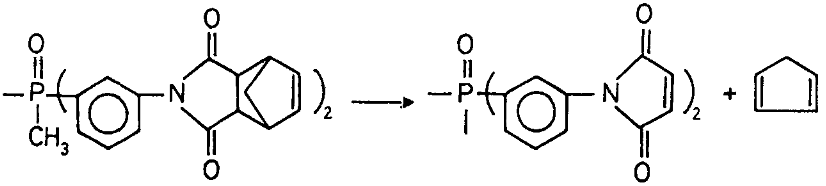
The polymerisation of ethynyl-terminated imides is basically a free radical propagation of ethyne moiety to a linear conjugated polyene [22–26]. The kinetic chain length of such reaction is usually short (6–8 ethynyl units).



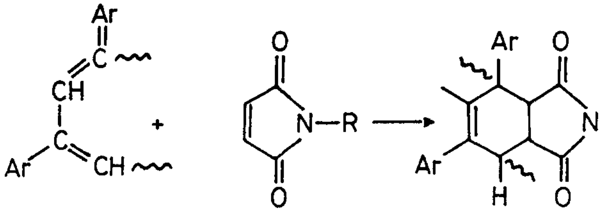
Several routes for crosslinking and aromatisation have been suggested for these resins [24–28].

Curing of nadicimide resins also comprises of several reactions such as endo-exo isomerisation, reverse Diels Alder reaction (RDA), polymerisation etc. The RDA reaction leads to the formation of cyclopentadiene and a substituted maleimide as depicted below:

Where n=6-8



It is quite likely that when ethynyl terminated imides are co-cured with nadicimide resins, then the maleimide derivative generated *in situ* undergoes Diels Alder reaction with conjugated polyene thereby enhancing the condensed phase reactions.



The higher char yields observed in some resin blends can thus be explained.

## References

1 A. O. Hanky and T. L. St. Clair, SAMPE J., 21 (1985) 40.
2 R. H. Pater, SAMPE J., 26 (1990) 19.
3 A. M. Thayer, Chem. Eng. News, 68 (1990) 37.
4 R. H. Pater and C. D. Morgan, SAMPE J., 24 (1988) 25.
5 R. S. Raghava, J. Polym. Sci., Part B, Polym. Phys., 26 (1988) 25.
6 R. H. Pater, Polym. Eng. Sci., 31 (1991) 20, 28.

7 P. A. Steiner, J. M. Browne, M. T. Blair and J. M. McKillen, SAMPE J., 23 (1987) 8.
8 J. D. Boyd and T. F. Biermann, Int. SAMPE Symp. Exhib. Proc., 32 (1987) 1386.
9 E. M. Woo, L. B. Chen and J. C. Seferies, J. Mater. Sci., 22 (1987) 3665.
10 M. K. Mikels and P. R. Schreiner, Int. SAMPE Symp. Exhib. Proc., 31 (1986) 501.
11 D. Landman, Natl. SAMPE Symp. Exhib. Proc., 28 (1983).
12 H. Zeng and K. Mai, Makromol. Chem., 187 (1986) 1787.
13 I. K. Varma and R. Sharma, Thermochim. Acta., 160 (1990) 209.
14 I. K. Varma and H. P. Mittal, Thermochim. Acta, 144 (1989) 339.
15 J. King, M. Chaudhri and S. Zahir, Nat. SAMPE Symp. 29 (1984) 392.
16 K. G. Garduner and M. S. Chattha, ACS Symp. Ser., 367 (1988) 660.
17 I. K. Varma and H. P. Mittal, J. Macromol. Sci. Chem., A 26 (1989) 937.
18 A. Mathur and I. K. Varma, Die. Angew. Makromol. Chem., 206 (1993) 53.
19 Sarfaraz Alam, L. D. Kandpal and I. K. Varma 'Proc. IX Nat. Symp. on Thermal Analysis, Ed. P. V. Ravindran, S. R. Bhardwaj, M. Sundersanan and S. R. Dharwadker, 1993, pp. 246.
20 Sarfaraz Alam, V. G. Jayakumari, L. D. Kandpal and I. K. Varma, 'Phosphorus containing nadicimide resins with amide linkages: Synthesis and Characterisation,' ISAMPE, Proc., 1993, pp. 37.
21 Sarfaraz Alam, L. D. Kandpal and I. K. Varma, 'Polymer Sciences, Recent Advances,' Vol. I, Ed. I. S. Bhardwaj, Allied Publ., 1994, pp. 260.
22 Sarfaraz Alam, L. D. Kandpal and I. K. Varma, J. Macromol. Sci., C33 (1993) 291.
23 Sarfaraz Alam, L. D. Kandpal and I. K. Varma, J. Appl. Polym. Sci., 53 (1994) 1073.
24 I. M. Pickard and I. J. Goldfrab, ACS Poly. Prepr., 20 (1979) 375.
25 M. D. Sefcick, E. O. Stejskal, R. A. McKay and J. Schaefery, Macromolecules, 12 (1979) 423.
26 P. M. Hergenrother, G. F. Sykes and P. R. Young, ACS Pet. Chem. Prepr., 24 (1973) 243.
27 P. F. Kovar, G. P. Ehlar and F. E. Arnold, J. Polym. Sci. Polym. Chem. Ed., 15 (1977) 1081.
28 A. G. Viehe (Ed.) Chemistry of Acetylenes, Dekker, New York 1969.