PII: S0032-3861(97)10366-4

Preparation and evaluation of composites from montmorillonite and some heterocyclic polymers. 1: Poly(*N*-vinylcarbazole)–montmorillonite nanocomposite system

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(Accepted 25 November 1997)

The cationic polymerization of *N*-vinylcarbazole (NVC) can be initiated directly by montmorillonite (MMT) The polymerization has been studied with MMT in solid phase and NVC at melting temperature ($> 64°C$) or in benzene solution at 50°C. By repeated benzene extraction of the PNVC–MMT reaction product, an intercalate of PNVC in MMT has been isolated. I.r. spectral analysis endorses the presence of PNVC in the intercalate. XRD analysis confirms expansion of d_{001} spacing of MMT indicating the intercalcation of PNVC in the MMT layer. TEM analysis indicates the particle size of PNVC–MMT intercalate to be 33 ± 10 nm. Thermogravimetric stability studies indicate, PNVC stability is much enhanced upon intercalcation confirming formation of intimately associated microaggregates of PNVC and MMT. Thus PNVC is completely lost around 700°C but PNVC–MMT composite undergoes 19.5% loss at 999°C the residue being MMT. From these t.g.a. data, it has been calculated that PNVC–MMT intercalate contains 6.35%. PNVC per gm of MMT. D.c. conductivity of PNVC–MMT composite (10^{-6} S/cm) is 10^{10} times greater than that for PNVC (10^{-16} S/cm). © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: poly(*N*-vinylcarbazole); montmorillonite; nanocomposite)

INTRODUCTION

Nanostructured composites based on clay[1,2] ultrafine oxides like colloidal silica[3], SnO_2[4], ZrO_2[5] and polymers from methylmethacrylate, styrene[1], acrylonitrile[1], pyrrole[2,3] or aniline[3,4] have been receiving much research attention in view of the many improved bulk properties of these composites in comparison to those of the base polymers. Notably, in all these preparations, clay mineral or the inorganic oxides have been used along with a free radical (acrylic monomers) or Lewis acid catalyst (pyrrole).

Among other potential polymer systems which could be expected to lead to nanocomposites of interesting properties the *N*-vinyls merit consideration. *N*-Vinylcarbazole (NVC) in this series is a well-studied monomer leading to a polymer (PNVC) of unusual electrical[6] and optoelectronic properties[6] and high thermal stability[6,7]. During the last decade, numerous attempts have also been made to chemically modify PNVC[7,8] to produce potential materials with improved bulk properties[7,8]. However, no attempt appears to have been made to prepare and evaluate PNVC-based nanocomposites This prompted us to explore PNVC intercalcated clay (montmorillonite, MMT) nano-composites.

In course of this work, we have made the significant observation that NVC in solid state or in nonaqueous solution can be directly polymerized by MMT alone at ambient or more effectively at elevated temperatures.

Further, a part of the resultant PNVC is retained in the MMT layers as an intercalate.

NVC is extremely prone to undergo carbocationic polymerization by charge-transfer complex[9] or by Lewis acids[6]. The kinetic and mechanistic aspects of these systems have been exhaustively explored. Of particular relevance from the point of view of the present system is the observation by Biswas and Maity that synthetic zeolites (13 $\times$ and SK500) and carbon black (CB) are capable of initiating NVC polymerization directly[10–12].

In this article, we wish to highlight the essential polymerization characteristics of NVC in molten state ($> 64°C$) and in benzene solution by MMT powder vis-a-vis the distinctive morphological thermostability and conductivity characteristics of PNVC intercalcated MMT.

A few comments are perhaps in order as to the end use possibilities of these nanocomposites. Unmodified PNVC and its charge-transfer complexes with various species have been successfully exploited for electrophotographic[13] and photosensitisation applications[13]. It would be of interest to explore whether these nanocomposites could be appropriately modified for use in these specific applications as costwise, cheaper materials. A favourable point in respect of these nanocomposites is their much improved dark conductivity. Introduction of potential polymers like PPY, PANI or PTF as conductive copolymers, interpenetrating network or blends in these PNVC-nanocomposites would be a challenging step towards the preparation of novel and cheap materials with modified antistatic[14], electromagnetic properties[14]. The research thus appears to be of wide scope, and further work in this series will be directed to this end.

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EXPERIMENTAL

Materials

N-Vinylcarbazole (BASF, Germany) was recrystallized from predistilled *n*-hexane and stored in dark. Montmorillonite, K-10, Sigma–Aldrich, USA, was dehydrated by drying for 3 days at 100°C and stored in a vacuum desiccator. All other chemicals and reagents were of analytical reagent grade and used after necessary purification by standard procedures.

Polymerization

Polymerization was carried out under two different conditions[15]: (i) bulk polymerization of NVC in presence of MMT at temperatures greater than the melting temperature (64°C) of NVC and; (ii) the solution polymerization of NVC in presence of MMT as a heterophase catalyst at 50°C.

Bulk polymerization. Known amounts of powdery MMT and NVC were taken in a stoppered Pyrex tube (20 ml) and polymerization was carried out at 70°C. The mass was then extracted with benzene and the precipitate was then filtered on a Gooch crucible, repeatedly washed with boiling methanol to remove unreacted monomer and dried at 60°C for 7 h.

Solution polymerization. A known amount of NVC was dissolved in a known volume of benzene and the solution was taken in a stoppered Pyrex tube (20 ml) containing a known quantity of powdery MMT. This mixture was then continuously stirred at 50°C for 1 h. The total contents of the tube were then added to requisite amount of methanol to precipitate the polymer which was processed as above.

Isolation of PNVC–MMT composite

The precipitate, thus isolated was expected to contain PNVC, a part of which might be adsorbed on the MMT surface, and a part intercalcated in the layers of MMT. Similar situations were also encountered by earlier workers[1] in various clay–polymer systems.

Dry PNVC–MMT composite was extracted with benzene with continuous stirring for various intervals of time till the extracts did not yield any precipitate in methanol. Finally, the total contents of the system were centrifuged and the centrifugate was separated from the residue. This procedure would remove all PNVC adsorbed on the surface but PNVC–MMT intercalate would remain unextracted. Blumstein confirmed by detailed experiments that for PMMA–clay composites benzene did not extract intercalcated PMMA[16]. In the present system, even after 2.5 h of continuous reflux in benzene, intercalcated PNVC could not be removed from MMT.

Characterization and property evaluation

I.r. spectra were taken on a Pye UNICAM SP3-300S Philips instrument. XRD analyses of MMT and PNVC–MMT intercalcates were performed on a Philips X-ray diffractometer Cu LFF 40 kV, 20 mA with wavelengths of 1.54060 and 1.54438. Surface morphologies of MMT and PNVC–MMT intercalcates were studied by taking scanning electron micrographs on a Hitachi S415A instrument. The particle sizes of MMT and PNVC–MMT composites were determined by transmission electron microscopy using a Hitachi 600 instrument. Thermogravimetric analyses of the polymers, MMT and PNVC–MMT composite were performed on a Stanton Redcroft STA 625 instrument. D.c. conductivity measurements were performed with a Keithley 617 solid-state electrometer using a cell containing a guard ring and stainless steel electrodes.

RESULTS AND DISCUSSION

### General features of polymerization

During polymerization beyond 50°C, there was a characteristic colour change in MMT from light gray to bluish green shade. This colour change was an indication for the onset of polymerization of NVC. This was, as expected, aided by an increase in temperature, since the polymerization rate would also be enhanced with temperature. A typical feature of the system was that simple contact between NVC and MMT would lead to the above colour change even at ambient temperature. Similar colour changes are a common feature with NVC-3d transition metal salt systems and are due to a change in the valence state of 3d centre upon complex formation. Characteristically, PNVC that was extracted with benzene, was a white powder, $n_{relative}$(benzene) = 1.2 and i.r. spectrum essentially similar to that for PNVC reported in the literature[17].

The reason for the use of higher temperature (50°C) for solution polymerization is that the process requires adsorption of NVC on the MMT surface. At room temperature, this will be low and will be expected to increase at higher temperatures. In fact, we realised *ca.* 10% yield in a day by room temperature polymerization.
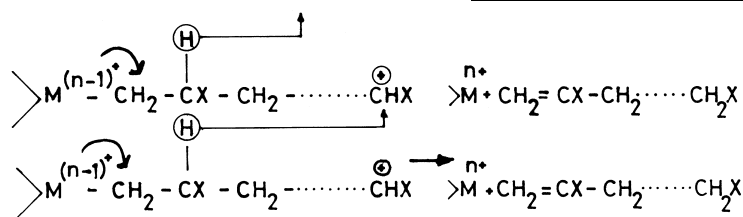
Figures 1 and 2 represent typical conversion time plots for the two aforementioned polymerization systems. In general, conversions are dependent on the amount of MMT up to 1 h of polymerization in the recipes used, and level off at higher times of polymerization. The data are reproducible within 3%–4%. which is noteworthy in view of the heterogeneous nature of the polymerization systems.

Mechanism of polymerization

As with the NVC–zeolite (13× and SK 500) systems[10–12], the initiation in the NVC–MMT system appears to be cationic, involving Brønsted acid sites in MMT arising through the dissociation of interlayer water molecules coordinated to the exchangeable cations[1]. Yet another possibility, especially with NVC, is that the transition
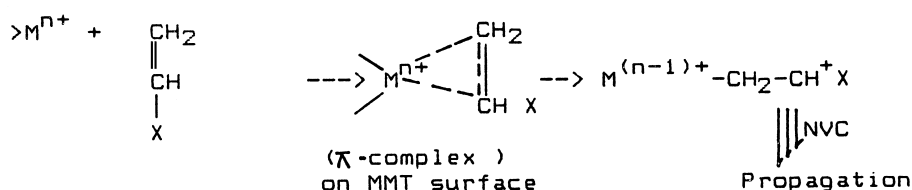
metal oxides Fe_2O_3, TiO_2 in MMT can also lead to cationic initiation of NVC as reported by Biswas and Maity[10–12]. Termination may be by proton transfer

Intercalcation of PNVC in the MMT layer

Table 1 represents some typical data on the retention of PNVC in the MMT layer after benzene extraction. These

or by impurities as adventitious water[18]. Typical colour change of MMT in the presence of NVC appears consistent with valency changes of transition metal ions[19].

The cationic initiation mode is also endorsed by the retardation of the polymerization by water, amines and thiophene[9].
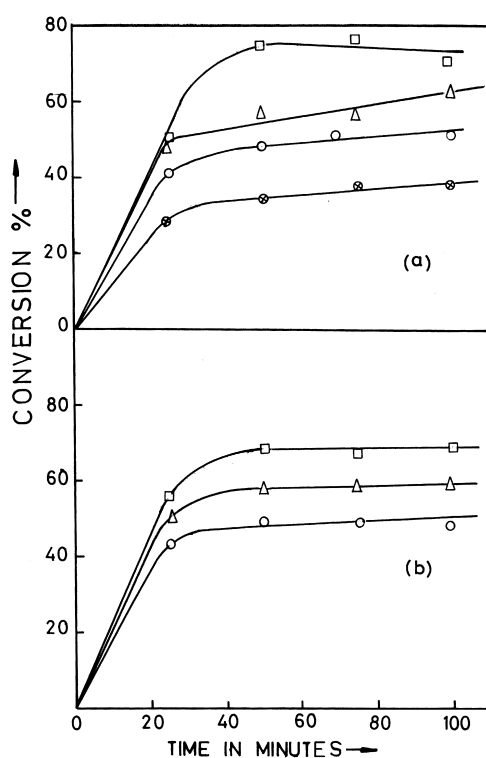
data (serial numbers 1–5, *Table 1*) indicate that the amount of PNVC remaining unextracted with benzene increases to a maximum of 20% and falls thereafter with further increase of MMT amount serial number 6, *Table 1*). Also the amount
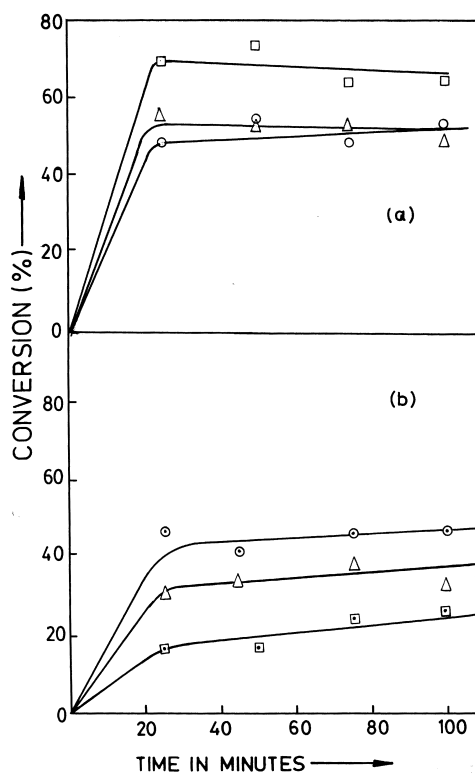
Figure 1 Conversion time plots for the polymerization of NVC melt by MMT. (a) NVC = 0.01 g; MMT = 0.01 g (⊗), 0.02 g (○), 0.03 g (△); 0.05 g (□). (b) MMT = 0.01 g; NVC = 0.02 g (○), 0.03 g (△), 0.05 g (□)

Figure 2 Conversion time plots for the polymerization of NVC (benzene solution) by MMT. (a) [NVC] = 0.1 M (0.096 g/5 ml benzene); MMT = 0.02 g (○), 0.03 g (△), 0.05 g (□). (b) MMT = 0.01 g; [NVC] = 0.026 M (⊡), 0.05 M (△), 0.1 m (◉)

Table 1 Retention of PNVC in the MMT layer

Experiment number	Weight of MMT (g)	% conversion to PNVC[ab]	% extracted with benzene[b]	% remaining unextracted with benzene[b]	% PNVC retained per g of MMT
1	0.02	55.00	53.70	1.30	2.8
2	0.03	56.00	54.04	1.96	3.3
3	0.05	70.00	66.80	3.20	4.2
4	0.10	73.30	63.30	10.00	7.3
5.	0.20	74.00	54.00	20.00	7.5
6	0.30	47.30	41.05	6.25	1.0
7[c]	0.10	94.00	92.50	1.50	—
8[c]	0.10	94.00	92.60	1.40	—

[a]In each case (nos. 1–6) polymerization was carried out at 50°C for 1 h; concentration of NVC solution = 0.1 mol; and volume of NVC/benzene solution = 5 ml
[b]Data represent average of three sets of experiments
[c]Conducted with preformed PNVC (0.09 g PNVC in 5 ml benzene, conversion 94%)
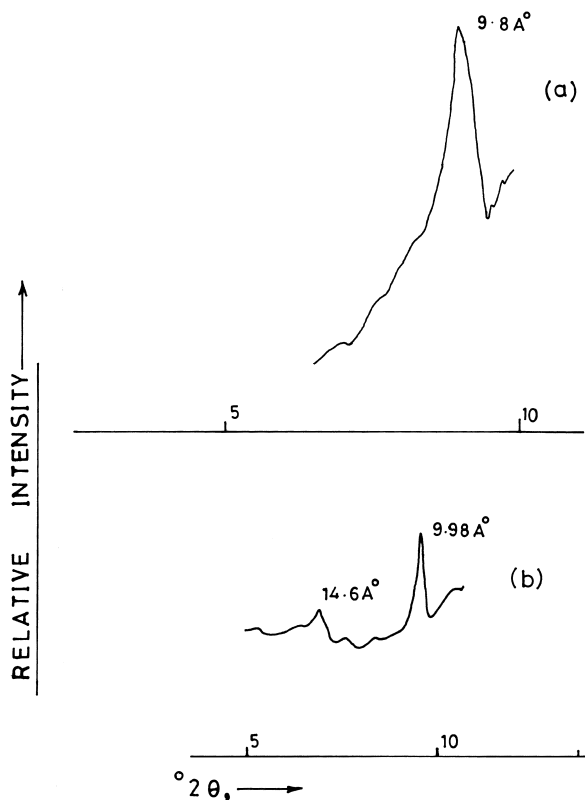
Figure 3 XRD pattern of (a) MMT and (b) PNVC–MMT composite

retained, runs almost parallel to the overall PNVC yield in the polymerization. For run number 6, with an MMT amount as high as 0.3 g, the yield of PNVC suffers a decrease from 74% to 47%. The initiation of NVC polymerization on the MMT surface involves adsorption of NVC molecules in the first place[19], followed by supply of NVC molecules at the propagation site. It may be that, with very high amounts of MMT, adsorption of NVC moieties will be favoured to a large extent, while supply of NVC

molecules at the propagation site will be eventually restricted leading to a fall in the conversion as actually observed.

An important feature is further revealed by the data of serial numbers 7 and 8 in *Table 1*, which show that negligible retention of PNVC occurs if preformed PNVC in benzene solution and MMT are stirred together for the same time as in the rest of the runs in *Table 1*. These results imply that retention occurs only when a part of the NVC monomer is in contact with MMT and eventually polymerized by it. It is likely that some NVC molecules will be adsorbed in the MMT lamellae, wherein initiation and propagation will follow almost concurrently. Thus, there will be two loci of polymerization—one in the MMT lamellae and the other on the MMT surface. The part undergoing polymerization in the MMT lamellae will represent the PNVC intercalcated in MMT or the composite. Our results on TEM analysis reveal that PNVC-intercalcated MMT is actually a nano-composite.

I.r. spectra

Comparison of i.r. spectra of MMT, PNVC–MMT and PNVC confirms inclusion of PNVC in the intercalate.

XRD analysis of PNVC–MMT composite

Figure 3a shows XRD pattern of MMT and *Figure 3b* that of the PNVC–MMT composite. As is well established[1,2], the peak at 14.6 Å can be ascribed to the d_{001} reflection of MMT-based intercalcates and that at 9.8–9.9 Å to that for pure MMT. This feature confirms that NVC moieties have actually penetrated the interlamellar spaces of MMT and eventually been polymerized therein to form the PNVC–MMT intercalate.

Scanning electron microscopic analysis

SEM pictures for MMT and PNVC–MMT composite, *Figure 4a* and *Figure 4b*, respectively, do not reveal any gross morphological differences between them. Overall particle arrangement appears to be more compact in MMT, while in the PNVC–MMT intercalate
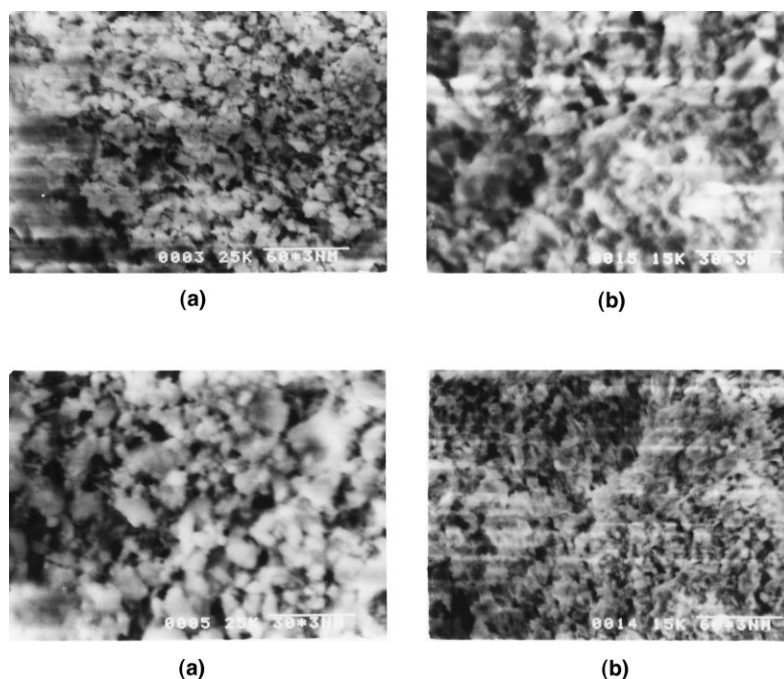

(a)

(b)

(a)

(b)

Figure 4 SEM photographs for (a) MMT and (b) PNVC–MMT composite

aggregates of particles appear to be somewhat more segregated or scattered producing gaps between the particles.

Transmission electron microscopic analysis of PNVC–MMT composite

Figure 5 represents two TEM photographs of the PNVC–MMT composite. The lighter region[5] in the background of the TEM picture is due to MMT, and the darker
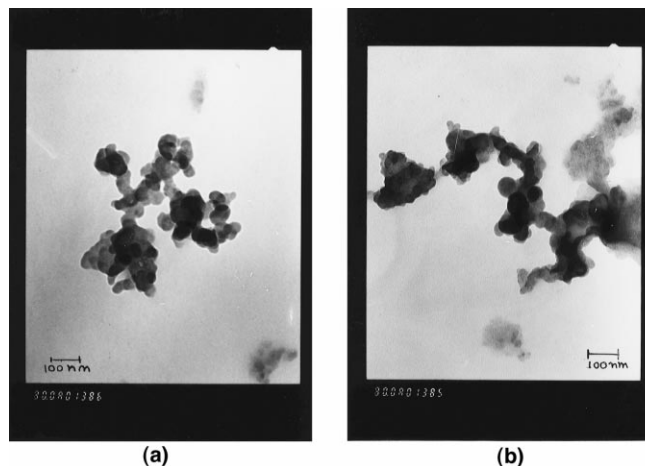
regions[5] are due to PNVC particles. The average particle diameter for the composite, as calculated from the TEM photographs, is 33 ± 9 and 33 ± 10 nm, respectively, in duplicate experiments. The distinct morphology of the PNVC–MMT nanocomposite, and its visual resemblance to the raspberry morphology of PPY–SiO$_2$ nanocomposites reported by Armes and co-workers[3,4], are to be noted.

Thermal stability characteristics

Figure 6a and Figure 6b represent typical weight loss *versus* temperature data for PNVC–MMT composite and MMT, respectively. Table 2 compares thermal stability of PNVC[20], PNVC–MMT composite and MMT. These data confirm that the thermal stability of PNVC is appreciably improved after intercalcation in the MMT layer. This is expected since the intercalcated matrix comprises intimately associated[5] particles of PNVC dispersed in the nanoaggregates of MMT. Beyond 999°C, the incombustible residues in Figure 6a,b are due to unintercalcated MMT nanoparticles. It is relevant to mention here that Armes and co-workers[3,4] reported similar thermal stability features for PPY–stringy silica and PANI–silica nanocomposites. In the present system, Figure 6b reveals that unintercalcated MMT resisters a total weight loss of 13.24% due to probable loss of volatile impurities. Figure 6a indicates that the PNVC–MMT intercalate loses 19.59% of mass which comprises loss of intercalcated PNVC along with the volatile impurities present in the system. Calculation in the line of
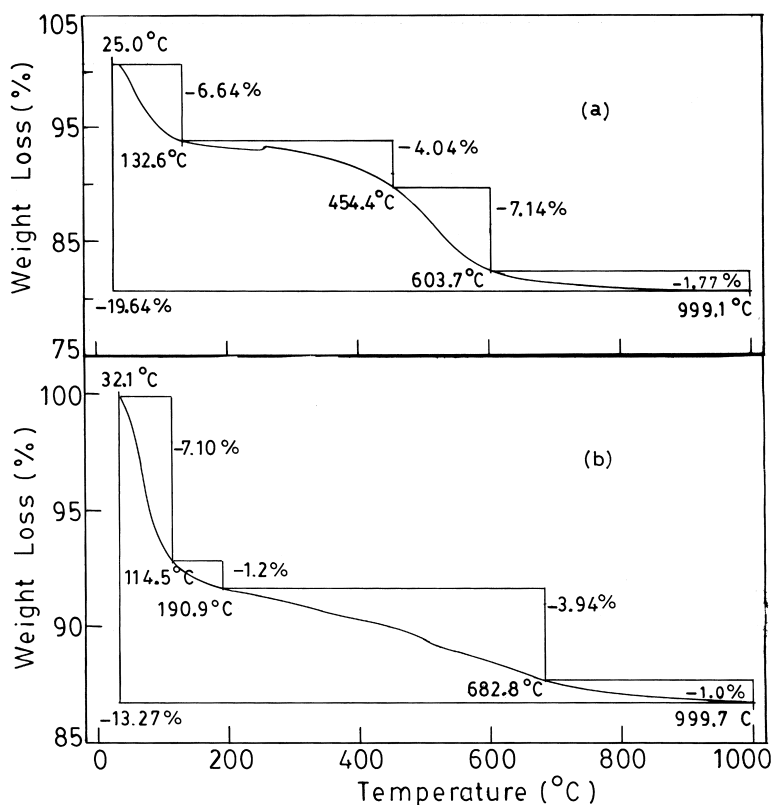

Figure 5 TEM photographs of PNVC–MMT composite (magnification, 80 000 ×)

Figure 6 Weight loss *versus* temperature thermogram for (*a*) MMT and (*b*) PNVC–MMT composite

Table 2 Weight loss *versus* temperature data for PNVC, PNVC–MMT composite and MMT

Materials	% weight loss (temperature (°C))		
PNVC[20]	8 (400)	75 (500)	Complete (700)
PNVC–MMT composite	10 (454)	17.7 (604)	19.5 (999)
MMT	8.3 (190.9)	12.2 (682)	13.2 (999.7)

Table 3 D.c. conductivity data of PNVC–MMT composite and PNVC

Materials	D.c. conductivity (S/cm)
PNVC–MMT composite	10^{-6}
PNVC[7]	10^{-16}

Armes et al.[3] will now indicate a PNVC layer of mass of 6.35% in the MMT layer. Interestingly, this figure compares reasonably well with the value of 7.3% for the PNVC retained per unit mass of MMT (*Table 1*). Relevantly, such a comparison could not be made by Armes et al.[3] for their PPY/PANI-based system because of the general intractability of these polymers.

D.c. conductivity

Table 3 compares the d.c. conductivity values of PNVC[7] and PNVC–MMT composite. Remarkably, conductivity of PNVC–MMT composite is enhanced 10^{10} times relative to that for PNVC. This feature is very significant since conducting composites based on PNVC have been reported only in few cases, such as with PNVC–carbon black (0.11–1.0 S/cm)[21] or with PNVC–PPY blends (3.3 × 10^{-6} S/cm)[17]. We hope to improve the conductivity further by chemical doping. It is relevant to mention in this context that similar enhancement in conductivity was reported for PPY–ZrO_2 nanocomposites[5] relative to that for unmodified PPY. This feature has been ascribed[5] to the formation of stronger PPY grains intimately associated with the ZrO_2 nanoparticles.

CONCLUSIONS

MMT is capable of initiating directly the cationic polymerization of NVC. The product comprises a benzene-extractable PNVC and a benzene-insoluble PNVC–MMT intercalate of particle size in the order of 33 ± 10 nm as revealed by TEM analysis. The PNVC–MMT nanocomposite is characterized by improved d.c. conductivity and thermostability relative to the base polymer.

ACKNOWLEDGEMENTS

REFERENCES

1. Akelah, A. and Moet, A., *J. Appl. Polym. Sci., Appl. Polym. Symp.*, 1994, **55**, 1994.
2. Akelah, A., Salahuddin, N., Hiltner, A., Baer, E. and Moet, A., *Nanostructured Materials*, 1994, **4**, 3.
3. Armes, S.P., Gottesfeld, S., Beery, J.G., Garzon, F. and Agnew, S.F., *Polymer*, 1991, **32**, 2325.
4. Maeda, S. and Armes, S.P., *Synthetic Metals*, 1995, **73**, 151.
5. Bhattacharyya, A., Ganguly, K.M., De, A. and Sarkar, S., *Mater. Res. Bull.*, 1996, **31**, 527.
6. Pennwell, R.C., Ganguly, B.N. and Smith, T.W., *J. Polym. Sci., Macromolecular Rev. (and references cited therein)*, 1973, **13**, 63.
7. Biswas, M. and Das, S.K., *Polymer*, 1982, **23**, 1705.
8. Biswas, M. and Mitra, P., *J. Appl. Polym. Sci.*, 1991, **42**, 1989; Biswas, M. and Majumder, A., *J. Appl. Polym. Sci.*, 1991, **42**, 2489; Mitra, M. and Biswas, M., *J. Appl. Polym. Sci.*, 1992, **45**, 1685.
9. Scott, H., Miller, G.A. and Labes, M.M., *Tetrahedron Lett.*, 1963, **17**, 1073.
10. Biswas, M. and Maity, N.C., *Adv. Polym. Sci.*, 1979, **31**, 47.
11. Biswas, M. and Maity, N.C., *J. Macromol. Sci. Chem.*, 1962, **A18**(3), 477.
12. Biswas, M. and Maity, N.C., *Polymer*, 1980, **21**, 1344.
13. Pearson, J. M., in *Concise Encyclopedia of Polymer Science and Engineering*, ed. J. Kroschwitz. Wiley, New York, 1990, p. 1240; Biswas, M. and Uryu, T., *J. Macromol. Sci., Rev. Macromol. Chem. Phy.*, 1986, **C26**, 249.
14. Omastova, M., Pionteck, J. and Pavlinec, J., in *Partnership in Polymers*. The Cambridge Polymer Conference 30th September–2nd October, 1996. Churchill College, University of Cambridge, 1996, p. 38.
15. Biswas, M. and Sinha Ray, S., Patent submitted through CSIR, New Delhi to the controller of Patents New Delhi, 1997.
16. Blumstein, A., *J. Polym. Sci., Part A*, 1965, **3**, 2653.
17. Biswas, M. and Roy, A., *European Polym. J.*, 1995, **31**, 725.
18. Biswas, M. and Chakraborty, D., in *Macromol. Revs.*, vol. 8, ed. G.B. Butler, K.F. O'Driscoll and M. Shen. Marcel Dekker, New York, 1972, p. 189.
19. Biswas, M., Maity, M. M. and Ganguly, N. D., *Die Macromol. Chem.*, 1969, **124**, 263; Biswas, M. and Mishra, P. K., *Die Macromol. Chem.*, 1973, **163**, 37.
20. Biswas, M. and Packirisamy, S., *J. Appl. Polym. Sci.*, 1982, **27**, 1823.
21. Biswas, M. and Roy, A., *Polymer*, 1994, **35**, 4470.