Anionic synthesis of poly(urethane-g-acrylonitrile)

K. Adibi, M. H. George and J. A. Barrie
Department of Chemistry, Imperial College of Science and Technology, London, SW7 2AY

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High molecular weight poly(ester-urethane) based on diphenyl methane-4,4′-diisocyanate (MDI), PU1, and also on toluene diisocyanate (TD1), PU2, have been metallated using sodium hydride in *N,N*-dimethylformamide, (DMF). Metallation was confirmed by coupling samples of metallated PU1 and PU2 with methyl iodide and the use of infra-red, and n.m.r. G.p.c. studies indicated that an increase in the percentage of metallation at about 0°C in DMF caused a decrease in the stability of the soluble metallated backbone polymer and was accompanied by degradation. An increase in temperature from 0° to 100°C of a 15% metallated polyurethane sample in DMF increased the extent of degradation. At 0°C, polymers with a degree of metallation of less than 50% were relatively stable. At about 0°C in DMF, acrylonitrile was successfully grafted by anionic polymerization following metallation of PU1 and the graft copolymers were readily separated by fractionation from small amounts of the homopolymer, polyacrylonitrile. The graft copolymers were characterized by microanalysis, solubility measurements, infra-red spectroscopy and viscometry. The vinyl monomers styrene, methyl methacrylate and vinyl acetate, and the cyclic monomers ethylene oxide, propylene oxide, *N*-methyl-2-pyrrolidone and hexamethylcyclotrisiloxane, could not be grafted anionically to the metallated polyurethane based on MDI.

INTRODUCTION

There is a good deal of current interest in the chemistry and technology of linear, branched, grafted and network polyurethanes, and numerous review articles and monographs have appeared[1–5]. Linear segmented polyurethanes, which are essentially block copolymers built up of hard and soft chain segments in an alternating fashion, exhibit many of the properties of crosslinked elastomers and are of particular importance[2,6].

However, relatively few polyurethane graft copolymers have been reported and most have been synthesized by free radical polymerization techniques[4,7,8]. Anionic grafting methods, using polyurethanes to generate the active polymeric anionic sites which subsequently initiate anionic polymerization have not been successfully applied, in spite of the fact that both the number of active sites and the graft lengths can be controlled[9,10]. Only the preliminary metallation of simple polyurethanes derived from ethylene glycol and MDI or TDI has been described in the literature[11].

This paper describes the metallation of some commercial poly(ester-urethane) samples based on MDI or TDI, and discusses the effect of increasing the percentage of metallation and temperature on the thermal stability of the metallated backbone. The reactivity of a metallated polyurethane based on MDI with respect to various monomers is reported and the successful synthesis and characterization of graft copolymers using acrylonitrile is also described.

EXPERIMENTAL

Reagents

Sodium hydride, NaH (Koch Light Laboratories Ltd.) was supplied as a 50% w/v dispersion in mineral oil which was miscible with DMF. Sodium hydride acts as a strong base in DMF and is suitable for the metallation of compounds containing ester groups without attack on the ester groups[12].

N,N-*Dimethylformamide (DMF)* (BDH Chemicals) was the solvent for the poly(ester-urethane) samples and was the usual reaction medium for metallation.

For purification it was dried over Linde 4A molecular sieve, fractionally distilled at low pressure from BaO and the middle fraction was retained. The presence of any free amine in DMF is undesirable and its absence was confirmed periodically using 1-fluoro-2,4-dinitrobenzene[13].

Acrylonitrile, (BDH Chemicals) was 99% w/w pure, stabilized with 0.005% w/w *p*-methoxyphenol, and was purified as previously described[14].

Methyl iodide (BDH Chemicals) was dried using anhydrous calcium chloride and was then fractionally distilled at atmospheric pressure, the middle fraction boiling at 42°C being retained.

Argon. Highly purified argon, 99.998% v/v (British Oxygen Co.) was passed through activated silica gel before use.

Poly(ester-urethane). The samples of poly(ester-urethane) used in this study, PU1 and PU2, were supplied by ICI Ltd, Organics Division. PU1 was a condensate of a polyester, diphenyl methane-4,4′-di-isocyanate, (MDI), and 1,4-butane diol, while PU2 was a condensate of approximately equimolar proportions of a polyester with toluene diisocyanate, (TDI). These polyurethanes were purified by dissolving each in THF, 5% w/v, and removing the additives by filtering the solution through a sintered glass funnel, (porosity 3).

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Each polymer was recovered by precipitation into a rapidly stirred mixture of methylated spirits and distilled water.

The white rubbery polymers were washed several times with distilled water and then dried in a vacuum oven at room temperature. Later the polymers were freeze-dried for two days from purified 1,4-dioxane, 5% w/v, while being protected from light by the use of aluminium foil.

Analysis

	Carbon (C)	Hydrogen (H)	Nitrogen (N)
PU1	62.74%	7.33%	3.06%
PU2	61.05%	8.19%	2.64%

Gel permeation chromatography, g.p.c.

G.p.c. measurements were carried out by the Polymer Supply and Characterization Centre, RAPRA, Shawbury, Shrewsbury, using THF as solvent.

Infra-red, i.r.

I.r. measurements were performed with a Perkin–Elmer 157G spectrophotometer using thin films of PU1, PU2 and *N*-substituted polyurethanes, cast from THF, and of graft copolymers cast from DMF.

Nuclear magnetic resonance (n.m.r.)

The spectra of the original and modified poly(ester-urethane) were recorded using a Varian XL-100-12 n.m.r. spectrometer, with fully deuterated DMSO as solvent.

EXPERIMENTAL

Metallation

Each metallation reaction was carried out under dried argon in a three necked round-bottom flask which had been flamed out before use. Care was taken to remove from reagents and apparatus any impurities containing active hydrogen, such as moisture, which could react with the NaH. The calculated amount of sodium hydride, according to the percentage of metallation required, was added by means of a rotating sample tube fitted with a cone to the three necked flask containing DMF (15 cm^3) cooled to about 0°C with a sodium chloride–ice bath.

Purified PU1 (2 g) which had been dissolved previously in DMF (40 cm^3) was added through a pressure equalizing dropping funnel to the dispersion of sodium hydride in DMF inside the flask, and the contents were stirred vigorously using a magnetic stirrer. Metallation under the argon atmosphere was rapid and after 5 min the solution had acquired a pale greenish–yellow colour. The reaction mixture was then stirred for a further 15 min.

Metallation was confirmed by an *N*-substitution reaction involving the addition of methyl iodide to a solution of 100% metallated polymer at 0°C under argon, with subsequent isolation of the *N*-methyl substituted polymer. I.r. and n.m.r. spectra of the initial polyurethane PU1 and the *N*-methyl derivative were recorded, and similar experiments were performed using PU2. Temperature, reaction time and degree of metallation were found to have a considerable influence on the stability of the metallated polyurethanes. Experiments designed to study these effects are described below.

Effect of temperature on the stability of the metallated polyurethanes.

Purified polymer PU1 (4 g) was metallated at 0°C to the extent of 15% based on the number of nitrogen atoms, previously established by microanalysis. After 15 min, the temperature was increased at an average rate of 1°C min^{-1} from 0° to 100°C. Samples of the metallated polymer solution under argon were withdrawn periodically. These samples were reacted with DMF containing a trace of nitric acid to regenerate the polyurethanes, which formed clear solutions.

Polyurethanes, in solution, removed at temperatures below 60°C were successfully recovered by reprecipitation into a methylated spirits–distilled water mixture, but polyurethanes removed from solution at 60°C and higher temperatures did not reprecipitate and had to be recovered by solvent evaporation under vacuum. Similar problems of reprecipitation were experienced when using the polyurethane PU2.

Effect of extent of metallation on the stability of the metallated polyurethanes

Purified polymer, PU1 (2 g) was metallated using NaH to the extent of 15% based on the number of nitrogen atoms in the polymer backbone. After metallation, the reaction was continued for further 1.75 h, while the temperature was maintained at about 0°C.

The polyurethane was regenerated by reacting the greenish metallated solution with DMF containing a trace of nitric acid. The solution became colourless and the polymer was then reprecipitated using a mixture of methylated spirits and distilled water. Subsequently the sample of polymer was dried in a vacuum oven at room temperature prior to g.p.c. analysis.

The above experiment was repeated under the same conditions but with 25, 40, 60 and 100% metallation.

Anionic graft copolymerization with acrylonitrile

Purified Polymer PU1 (2 g) was 15% metallated at 0°C under argon as described previously, using sodium hydride (0.03 g). After 10 min, all the sodium hydride had been consumed and the greenish-yellow colour of the metallated polymer gradually appeared. Purified acrylonitrile (4 cm^3) was added to the metallated polymer solution at about 0°C and the solution was stirred for 0.5 h. The solution became increasingly yellow during this time and the living graft copolymer and smaller quantities of living polyacrylonitrile were terminated with DMF/HNO_3 when the yellow solution became lighter in colour. The mixture of polymers was precipitated into distilled water, isolated by filtration and the mixture of polymers was then dried under vacuum at room temperature. The grafted polymers were isolated quite simply from the mixtures by fractional precipitation involving the progressive addition of non-solvent[15]. DMF was used as solvent and methylated spirits as non-solvent, and four fractions of highly swollen graft copolymer were obtained. Each of these fractions was redissolved in DMF and purified by reprecipitation into a large excess of a rapidly stirred mixture of methylated spirits and distilled water. The highest molecular weight fraction of this graft copolymer was characterized by microanalysis, viscosity, solubility and i.r. measurements.

The experiment was also repeated using different amounts of acrylonitrile (1, 2, 8, 10 cm^3) with PU1 at a fixed 15% metallation, in order to give different graft chain lengths. The highest molecular weight fraction of each graft polymer was retained for further study.

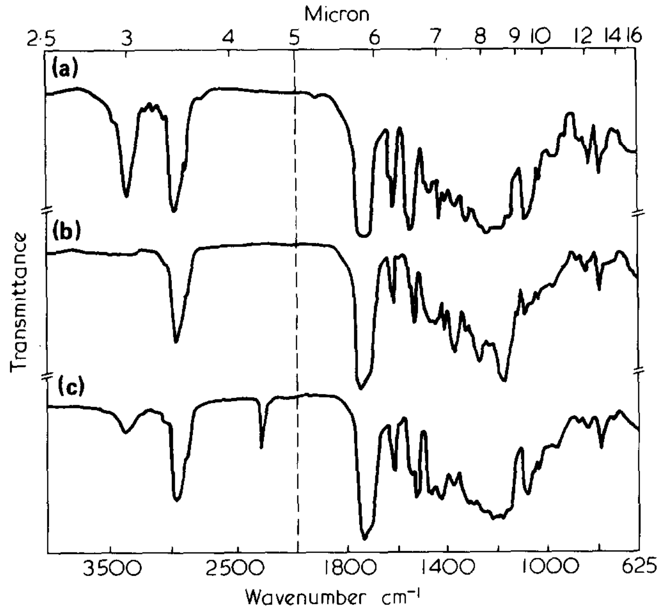


Figure 1 Infra-red spectra of (a) the original poly(ester-urethane), PU1; (b) the *N*-methyl derivative of PU1; (c) poly(urethane-g-acrylonitrile) based on PU1

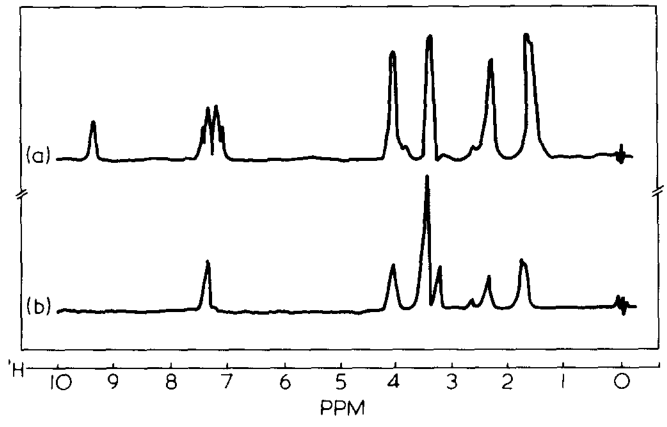
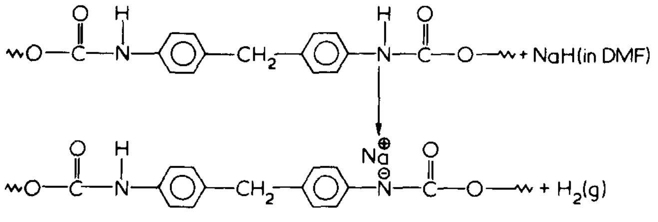


Figure 2 N.m.r. spectra of (a) the original poly(ester-urethane), PU1; (b) the *N*-methyl derivative of PU1

RESULTS AND DISCUSSION

The metallation experiments previously described indicated that polyurethanes containing ester groups can be successfully metallated using sodium hydride in DMF solution at 0°C under conditions outlined in the first experimental procedure. Attack of NaH on the ester function and subsequent degradation appears minimal and a similar absence of attack has been previously postulated for small molecules containing ester groups[9]. The metallated polyurethanes PU1 and PU2 formed homogeneous solutions in DMF and the pale yellowish-green colour was characteristic of their corresponding polymeric anions. For polyurethane PU1, the metallation reaction may be written in terms of one reactive centre in the polymer, most simply as:



assuming that one of the hydrogen atoms of this reactive segment is replaced.

Proof of metallation was established by coupling the polymeric anions from 100% metallated PU1 with methyl iodide at 0°C and isolating the *N*-methyl substituted polymer. *Figure 1* shows typical i.r. results for the original polymer PU1, spectrum (a), and the *N*-methyl derivative, spectrum (b). The absorption band of the –NH bond at 3340 cm^{-1} is clearly reduced in intensity following substitution. *Figure 2* shows the corresponding n.m.r. spectra for the original polymer PU1 and its *N*-methyl derivative.

The i.r. spectra of PU2 and its *N*-methyl derivative, prepared in a similar way to that of PU1, are shown in *Figure 3*.

Degradation of the metallated polyurethanes depends on factors such as the temperature of the solvent medium, the extent of metallation and time. *Figure 4a* shows a plot of the number-average molecular weight, $\bar{M}_n$ of regenerated polyurethane PU1 obtained by g.p.c. against the temperature at which the metallated polymer was withdrawn from the DMF solution, as described in the second experimental procedure. *Figure 4b* shows the corresponding $(\bar{M}_w/\bar{M}_n)$ ratios, also determined by g.p.c. The polyurethane sample had initially been 15% metallated and the results indicate that up to about 20°C, under these conditions, the metallated PU1 was relatively stable. At about 40°C, however, rapid thermal degradation of the metallated polymer occurred with a corresponding dramatic decrease in molecular weight. The high value of $(\bar{M}_w/\bar{M}_n)$, shown in *Figure 3b* for the polymer

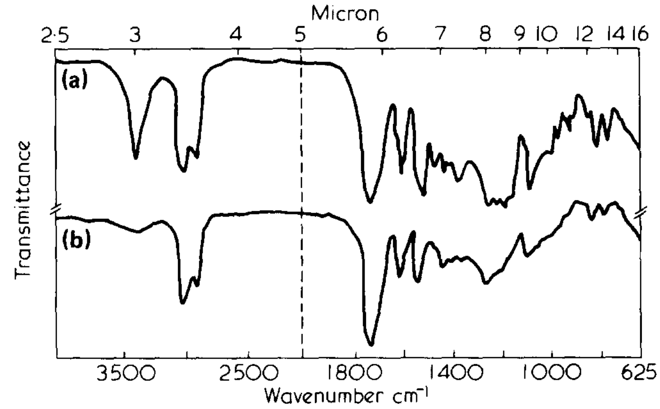


Figure 3 Infra-red spectra of (a) the original poly(ester-urethane), PU2; (b) the *N*-methyl derivative of PU2

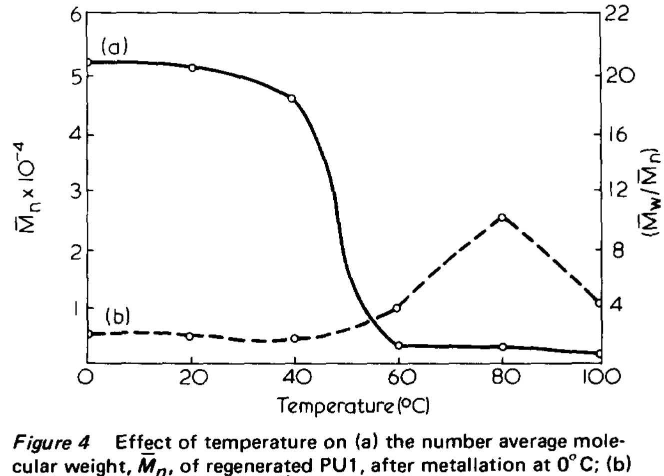


Figure 4 Effect of temperature on (a) the number average molecular weight, $\bar{M}_n$, of regenerated PU1, after metallation at 0°C; (b) the corresponding value of $(\bar{M}_w/\bar{M}_n)$

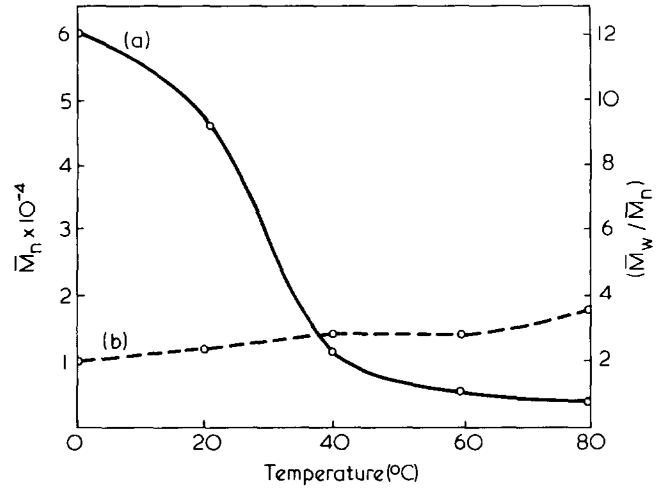
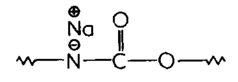
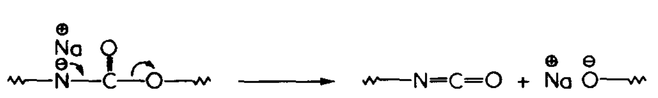


Figure 5 Effect of temperature on (a) the number average molecular weight, $\bar{M}_n$, of regenerated PU2, after metallation at 0° C; (b) the corresponding value of $(\bar{M}_w/\bar{M}_n)$

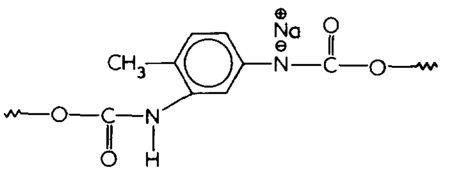
removed at 80°C may indicate that some reactions other than those of degradation occur in this system. The limiting value of the molecular weight of regenerated PU1 in this experiment was about 2500 and the instability of the metallated polyurethane was due to the presence of the metallated sites


$$\sim\!\!\sim\overset{\overset{\oplus}{Na}\,\ominus}{N}-\overset{\overset{O}{\|}}{C}-O\sim\!\!\sim$$

The final molecular weight is probably, therefore, that of the polyester segments with relatively small units of polyurethane attached. The precise mechanism of the degradation of PU1 may be quite complex, however, and some degradation of the unmetallated polyurethane segments may also be involved[2]. The i.r. spectra of the regenerated PU1 samples, isolated by evaporation of the DMF under high vacuum, before reprecipitation showed no evidence of a high concentration of $-N{=}C{=}O$ groups. This suggests that the mechanism of main chain scission of the metallated polymers does not occur solely by the simple process:


$$\sim\!\!\sim\overset{\overset{\oplus}{Na}\,\ominus}{N}-\overset{\overset{O}{\|}}{C}-O\sim\!\!\sim \longrightarrow \sim\!\!\sim N{=}C{=}O + \overset{\oplus}{Na}\,\overset{\ominus}{O}\sim\!\!\sim$$

The results obtained from the second experiment using 15% metallated PU2 are summarized in *Figure 5a* and *5b* for the TDI-based metallated polyurethane. Rapid degradation occurred at 20°C, indicating that a metallated site such as

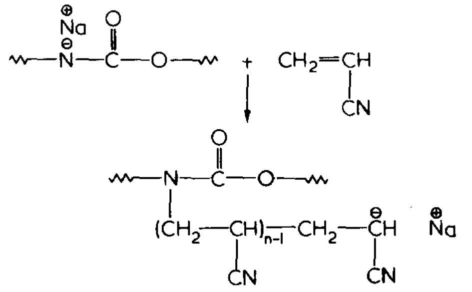


is more unstable than a metallated site from PU1. Presumably this effect is associated with the increase in negative charge on the N^- atom of the metallated PU2, due to the presence of the methyl group in the neighbouring aromatic ring. However, no great variation of $(\bar{M}_w/\bar{M}_n)$ ratios was observed during this degradation.

Further experiments established that for a sample of PU1 in DMF at 20°C an increase in time above 2 h caused a progressive decrease in molecular weight. After 24 h at 20°C, it was impossible to recover the degraded polymer by normal reprecipitation methods.

The results of the third procedure experiments are summarized in *Figure 6a* and *6b*. For a fixed time at 0°C, it is apparent that an increase in metallation above about 50% results in polymer instability and a rapid decrease in molecular weight, although the value of $(\bar{M}_w/\bar{M}_n)$ remains almost constant. This suggests that a process of random main chain scission occurs particularly at higher degrees of metallation.

The graft copolymers of the polyurethane PU1 were prepared and isolated as outlined in the fourth experimental procedure. Each living graft copolymer was formed by addition of acrylonitrile to the metallated centres and was yellow in colour:



A characteristic feature of the terminated copolymer dissolved in DMF was that the solution became increasingly yellow, even at room temperature, presumably due to degradation of the polyacrylonitrile grafts. A similar type of behaviour has previously been noticed for poly(hexamethylene adipamide) grafted with acrylonitrile[16]. The small amounts of relatively low molecular weight polyacrylonitrile formed in these experiments were probably produced by a process of chain transfer involving the living graft anion and monomeric acrylonitrile. Separation of the homopolymer from the graft copolymer was uncomplicated, due to the large differences in molecular weights of the graft copolymer and homopolymer and their different solubility characteristics.

Microanalytical results for the graft copolymer prepared from a 15% metallated sample of PU1, designated GPU1, showed an increase in nitrogen content as expected:

	Carbon (C)	Hydrogen (H)	Nitrogen (N)
PU1 found %	62.74	7.33	3.06
GPU1	63.14	6.84	7.98

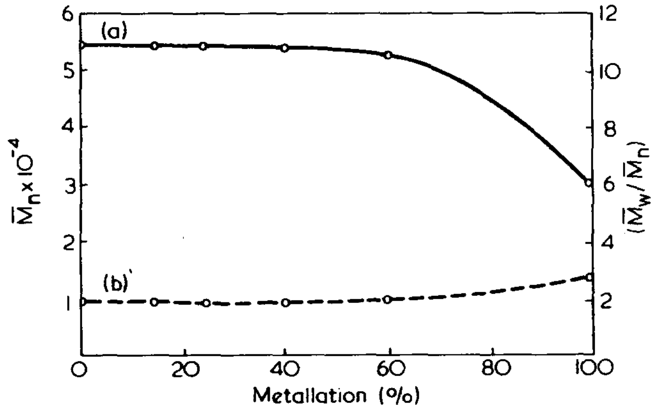


Figure 6 Effect of % metallation on (a) the number average molecular weight, $\bar{M}_n$, of PU1 after regeration; (b) the corresponding value of $(\bar{M}_w/\bar{M}_n)$

Table 1 Solubility characteristics of PU1 and GPU1

	PU1	GPU1
DMF	4	4
THF	3	0
DMSO	4	4
Benzene	1	2
Dioxan	3	0
Chloroform	3	1
Alcohol	0	0

0 = insoluble; 1 = swollen; 2 = soluble at 60°C; 3 = slightly soluble at room temperature; 4 = highly soluble at room temperature

This corresponds to about 21% w/w polyacrylonitrile in GPU1. The solubility of samples of PU1 grafted with polyacrylonitrile in different solvents depends both on the graft lengths and the graft frequency. Typical solubility results are shown in *Table 1* for the graft copolymer GPU1.

The limiting viscosity numbers of PU1 and GPU1 in DMF at 30°C were 0.86 cm^3/g and 0.54 cm^3/g respectively. These preliminary results suggest that the grafted molecules in DMF may be in a more collapsed state than molecules of PU1.

Attempts to graft monomers such as styrene, methyl methacrylate, vinyl acetate, ethylene oxide, propylene oxide, *N*-methyl-2-pyrrolidone and hexamethylcyclotrisiloxane at 0° to 40°C using a 15% metallated sample of PU1 proved unsuccessful. This was presumably due to the unreactive nature of the metallated sites, the high activation energy of the initiation step and possibly also steric effects.

Further work is proceeding to characterize the polyurethane-g-acrylonitrile samples and grafting using other monomers is under investigation.

ACKNOWLEDGEMENTS

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