

Block Copolymerization of Poly(ethylene glycol) and Methyl Acrylate Using Potassium Diperoiodatocuprate(III)

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ABSTRACT: Block copolymers of methyl acrylate (MA) and poly(ethylene glycol) (PEG) have been obtained using a novel redox system—potassium diperoiodatocuprate(III)[DPC]/PEG system in alkaline aqueous medium. Block copolymers with a high percentage of blocking were obtained, which indicated that the DPC/PEG redox system was an efficient initiator for this blocking. Effects of different conditions (concentration of reactants, temperature, concentration of the DPC, and reaction time) on the total conversion, percentage of blocking, and intrinsic viscosity were examined. The effects of different monomers and various

PEGs with different molecular weight on the total conversion were also examined. A mechanism is proposed to explain the generation of radicals and the initiation of block copolymerization. Some basic properties of the block copolymers were also studied by thermogravimetry and scanning electron microscope. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 2139–2145, 2005

Key words: diperoiodatocuprate; methyl acrylate; polyethers; initiators; copolymerization

INTRODUCTION

There are many reports on the synthesis of block copolymers in the literature. Hillmyer¹ generalized the methods for the preparation of di- and tri- block copolymers, including ionic polymerization, free radical polymerization, and metal-catalyzed polymerization. In these three methods, ionic polymerization was mostly used. However, due to the rigor condition and the narrow range of the monomer, the application of ionic polymerization in the chemistry industry is limited to some extent. Recently, chemical scientists have focused on free radical block copolymerization, because the reaction condition of radical polymerization was mild and the range of monomers is wide.

So far, radical block copolymerization of PEG with various vinyl monomers has been carried out by many authors. There is not only important meaning in theoretical studying, but also vast foreground for application. For example, textile layer pastern of polyacrylate is one of the commonly used layer pasterns now. It has many advantages, but its hygroscopic power is poor. Through block copolymerization, the hygroscopic power of polyacrylate layer pastern can be improved greatly.

Now, the commonly used initiators are Ce(IV)^{2,3} and Mn(III).^{4–6} Although ceric ion is an excellent ini-

tiator, its high price and acid medium limits its application. Therefore, to find new supernormal valence transition-metals as oxidants and polymer as a reductant to form a redox initiating system is very important in the synthesis of block copolymers.

During recent years, we have obtained some achievements on polymerization initiated by supernormal valence transition-metals, such as diperoiodatocuprate(III),^{7–9} diperoiodatoargentate(III),^{10,11} and diperoiodatonickelate(IV).^{12–15} It has been demonstrated that DPC is an efficient initiator. This paper investigated the block copolymerization of MA with PEG using DPC in an alkaline solution. The effects of variables on the blocking were studied in detail. The block copolymers were also characterized.

EXPERIMENTAL

Materials

The stock solution of DPC was prepared by the method given by Chandra and Yadava.¹⁶ The concentration of DPC was obtained by its absorption at $\lambda = 414$ nm using a Shimadzu UV-265 spectrophotometer (Japan). MA, analytical reagent, were obtained distilled from Huadong Reagent Factory (Tianjin). Poly(ethylene glycol) (PEG-6000) (Senchang Reagent Factory, Tianjin) was used as supplied. The other reagents were all of analytical reagent and used as received.

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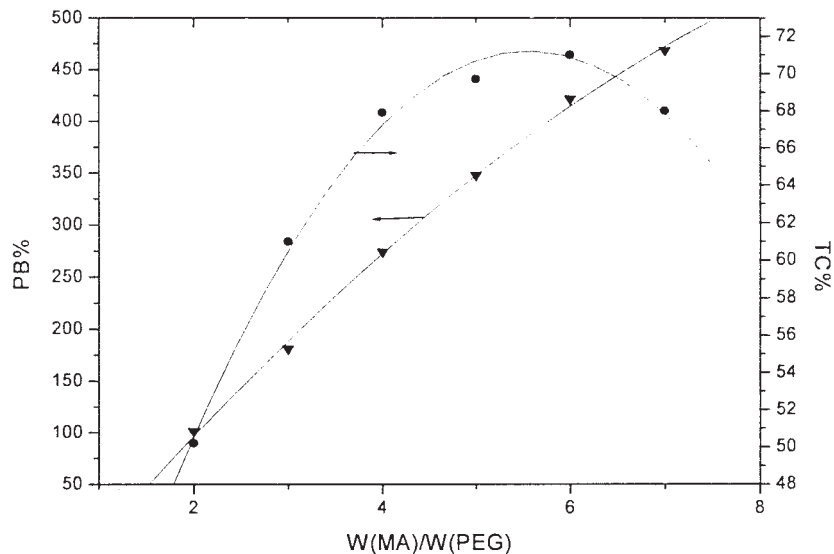


Figure 1 [DPC] = 2.106×10^{-5} mol/L, $T = 313$ K, Time = 60 min.

Experimental procedure

Required amounts of PEG-6000, MA, and water were placed in the reaction tube, degassed by flushing with pure nitrogen, and the reaction system was maintained at $30 \pm 0.1^\circ\text{C}$ in a thermostatic reservoir. Appropriate amounts of DPC were then added under nitrogen. After reaction for a period of time, the reaction was arrested by adding hydrochloric acid. The resultant polymer was filtered through a weighted sintered glass crucible, washed well with water, and then dried under vacuum to constant weight.

The blocking parameters, such as total conversion (TC) and percentage of blocking (PB) were defined and calculated as follows:

$$\text{TC \%} = (\text{weight of PMA} / \text{weight of MA charged}) \times 100$$

$$\text{PB \%} = (\text{weight of PMA} / \text{weight of PEG}) \times 100$$

To examine the effects of weight ratio of MA/PEG and [DPC] on intrinsic viscosity $[\eta]$, the intrinsic viscosities

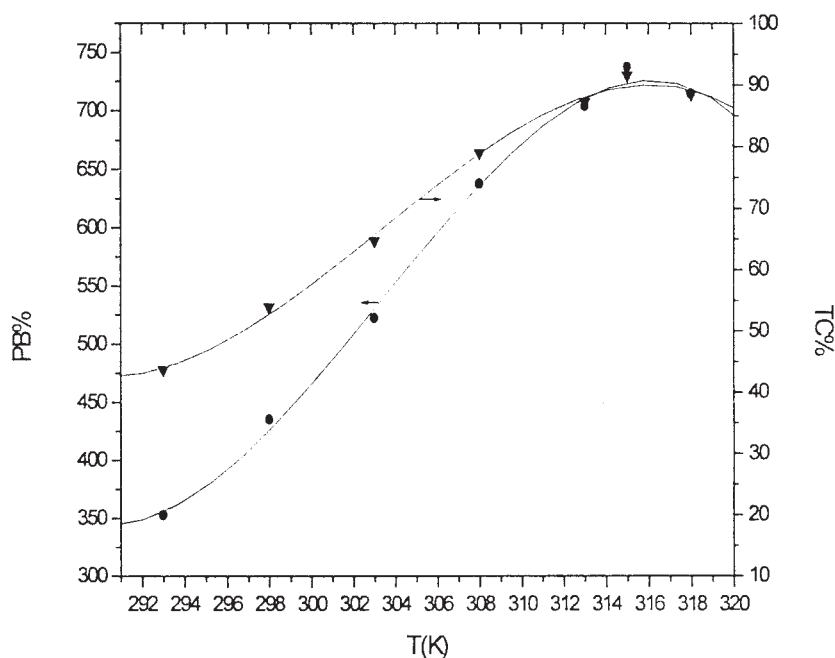


Figure 2 [DPC] = 2.106×10^{-5} mol/L, $W(\text{MA})/W(\text{PEG}) = 8$, Time = 60 min.

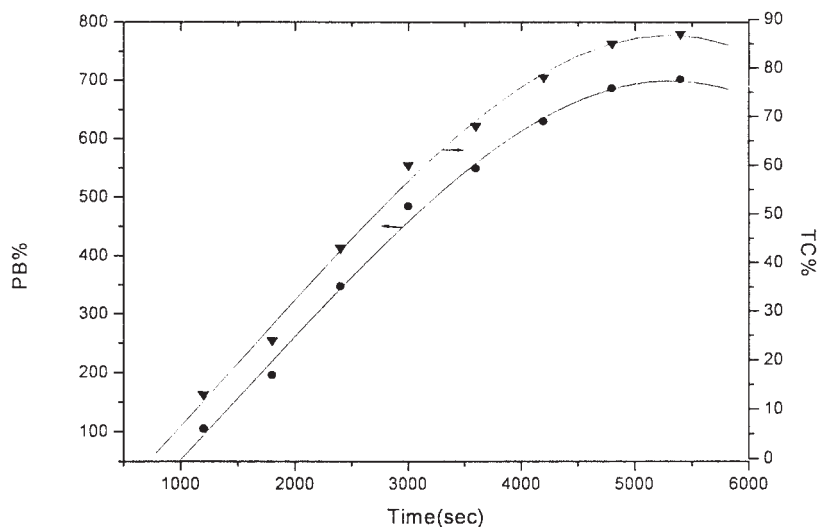


Figure 3 $[DPC] = 2.106 \times 10^{-5} \text{ mol/L}$, $W(\text{MA})/W(\text{PEG}) = 8$, $T = 313 \text{ K}$.

of copolymers were measured in DMF at 30°C. The measurements were carried out by dilution method, using a Cannon-Ubbelohde viscometer.

Measurements

FT-IR spectroscopy. The FT-IR spectra of PEG and block copolymer were recorded on an FTS-40 spectrometer (BIO RAD Co., USA) using a potassium bromide pellets technique.

$^1\text{H-NMR}$ spectroscopy. The $^1\text{H-NMR}$ spectroscopy of block copolymer was obtained from CDCl_3 solution on a Argonaut DPX-400 NMR spectroscopy.

SEM. Scanning electron microscope, AMKAY-1000B was used to observe the morphologies of PEG and the block copolymer.

Thermal analysis. TGA curve of the block copolymer was carried out on a Shimadzu apparatus (DGC-40 DTA-TG) at a heating rate of 10°C/min in a static air atmosphere.

RESULTS AND DISCUSSION

Effect of weight ratio of MA/PEG on blocking parameters

When keeping all other variables unchanged, the effect of weight ratio of MA/PEG on the block parameters was investigated. The results are shown in Figure 1. It can be seen that TC increased with an increasing weight ratio of MA/PEG at first and then declined. However, PB increased all along in the range studied.

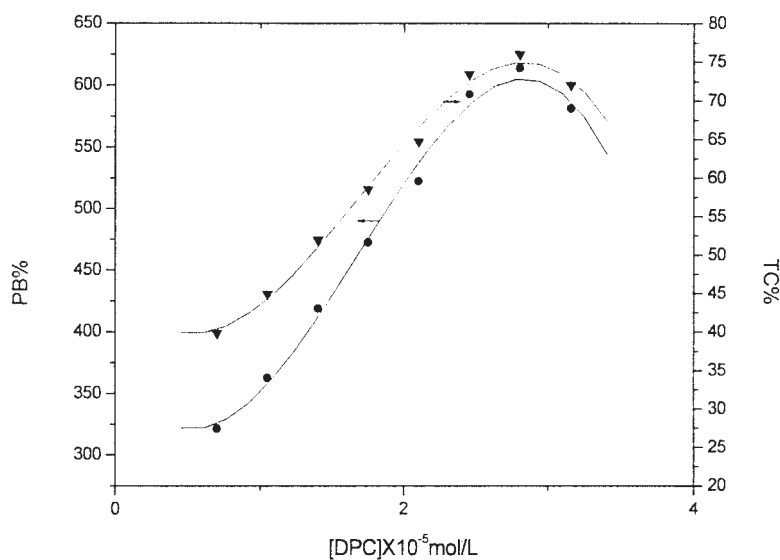


Figure 4 $W(\text{MA})/W(\text{PEG}) = 8$, Time = 60 min, $T = 313 \text{ K}$.

TABLE I
Effect of Different Monomers of Polyacrylate and Various PEGs with Different Molecular Weights on Conversion

Monomer ^a	Conversion (%)	PEG ^b	Conversion (%)
MA	92	1000	91
MMA	54	2000	86
EA	43	4000	78
MbuA	— ^c	6000	68

^a W(monomer)/W(PEG) = 8, [DPC] = 2.106 × 10⁻⁵ mol/L, time = 90min.

^b W(MA)/W(PEG) = 8, [DPC] = 2.106 × 10⁻⁵ mol/L, time = 60min, T = 313 K.

^c The reaction did not take place.

The declined trend of TC at a higher monomer amount may be explained as follows: Cu(III) in an aqueous phase relatively increases with the amount of MA increased when total volume was fixed. So the PB increased at all time, but the increment of PMA, related to the weight of MA added, it decreased. Namely TC declined.

Effect of temperature on blocking parameters

The relationship between temperature and TC as well as PB was investigated and shown in Figure 2. It can be seen that the TC and PB showed a similar trend, which increased with the rise of temperature at first and then increased slowly and even declined at higher temperatures. The tendency of lower TC and PB at higher temperature may be ascribed to a faster termination rate of the growing chain through oxidation by DPC, which, in reverse, accelerated the consumption of the DPC.

Effect of the reaction time on blocking parameters

When the other reaction conditions were invariable, the effect of reaction time on TC and PB was investigated and shown in Figure 3. The initial increase in the TC and PB clearly indicated that both DPC and macroradicals could keep its activity for a period of time. The following trend of leveling off can be attributed to the decrease in monomer concentration and initiator concentration.

Effect of DPC concentration on blocking parameters

Figure 4 shows the effect of initiator concentration on TC and PB. It can be seen that TC and PB increased significantly first, passed through a maximum, and then decreased. The initial increasing trend may be a result of the increased rate of polymerization, which can be ascribed to the formation of a great number of

TABLE II
Effect of String on Conversion

Time (min)	30	40	50	60	70
TC%(string)	10.2	25.4	41	50	56.5
TC%(unstring)	24.3	43	60	68	78

[DPC] = 2.106 × 10⁻⁵ mol/L, W(monomer)/W(PEG) = 8, T = 313 K

Rotation speed = 500 cycles/s

free radicals through an oxidation by DPC. However, an abundance of primary radicals may accelerate the rate of termination by coupling. At the same time, an excess of DPC may also increase the chance of encounter between DPC and propagating chain radicals, which will also terminate the reaction.

Effect of different monomers of polyacrylate and various PEGs with different molecular weights on conversion

It can be seen from Table I that conversion of the MA was the highest. It follows the order: MA > MMA > EA > MBuA. This may be attributed to solubility in the water of the MA being better than the others, so the MA has a greater chance to touch the PEG. It can be seen that conversion of the MA was the highest when PEG-1000 was used. This can be ascribed to the greater amount of hydroxyl in PEG-1000 at the same weight.

Effect of string

The total conversion under the unstirred condition was found to be greater than those under stirred conditions and the results are shown in Table II. The decreased rate under the stirred conditions may be due to the greater probability of encounters between the chain radical and the terminating agent, making the disappearance rate of the free radicals increase, therefore causing the decline of TC.

TABLE III
Effect of the Weight Ratio of MA/PEG and [DPC] on Intrinsic Viscosity [η]

MA/PEG ^a (W)	[η]dl/g	[DPC] × 10 ⁻⁵ mol/L ^b	[η]dl/g
5	0.0035	1.053	0.339
6	0.165	1.404	0.330
7	0.283	1.755	0.319
8	0.310	2.106	0.312
9	0.471	2.457	0.31
10	0.517	2.808	0.303
		3.159	0.301

^a [DPC] = 2.106 × 10⁻⁵ mol/L, T = 313 K, Time = 60 min.

^b W(MA)/W(PEG) = 8, Time = 60 min, T = 313 K.

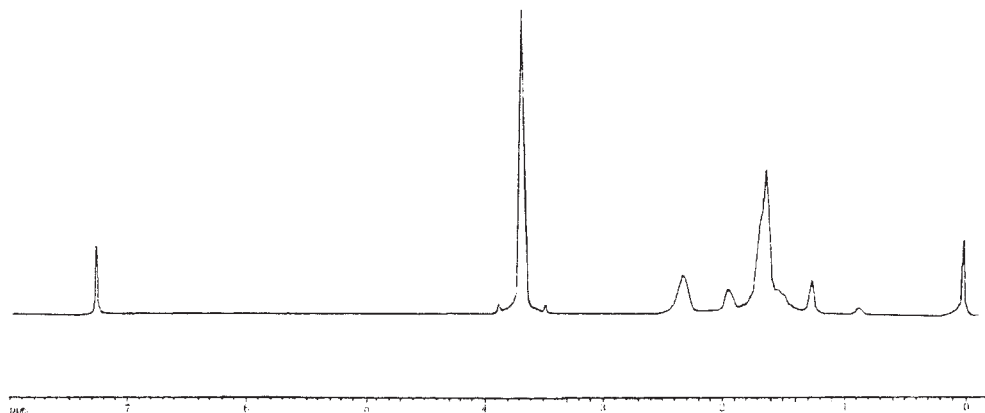


Figure 5 $^1\text{H-NMR}$ spectrum of PMA-PEG-PMA block copolymer.

Effect of the weight ratio of MA/PEG and [DPC] on intrinsic viscosity $[\eta]$

As shown in Table III, the intrinsic viscosity increased with the increased weight ratio of MA/PEG and decreased with the increased [DPC]. This is in agreement with the common rule of radical polymerization.

Proof of blocking

$^1\text{H-NMR}$ spectra in Figure 5 confirm the structures of the copolymers obtained: 3.55–3.75 ppm for the $-\text{[CH}_2\text{CH}_2\text{O]}_n-$ protons, 3.6 ppm for $-\text{OCH}_3$, and 1.8–1.9 ppm for $-\text{CH}_2-$. We can see from the picture, the peak of PEG chain protons superimposes that of

$-\text{OCH}_3$, but there are two small peaks around the main peak. This may be the result of interaction of the $-\text{CH}_2-\text{CH}_2-$. Therefore, it confirms that PEG and PMA have successfully copolymerized. The IR spectra of PEG, and block copolymer were recorded to further confirm the incidence of blocking. As shown in Figure 6, the absorption band at 3450 cm^{-1} can be assigned to the unreacted $-\text{OH}$ of the PEG segment. The bands at 2950 and 1400 cm^{-1} are due to C-H_{atr} and C-H_{def} of $-\text{CH}_2-$. Absorption at 1125 cm^{-1} is due to C-O_{str} of PEG. A sharp peak at 1750 cm^{-1} , corresponding to $>\text{C}=\text{O}$, is a clear indication of the presence of the PMA segment in the block copolymer.

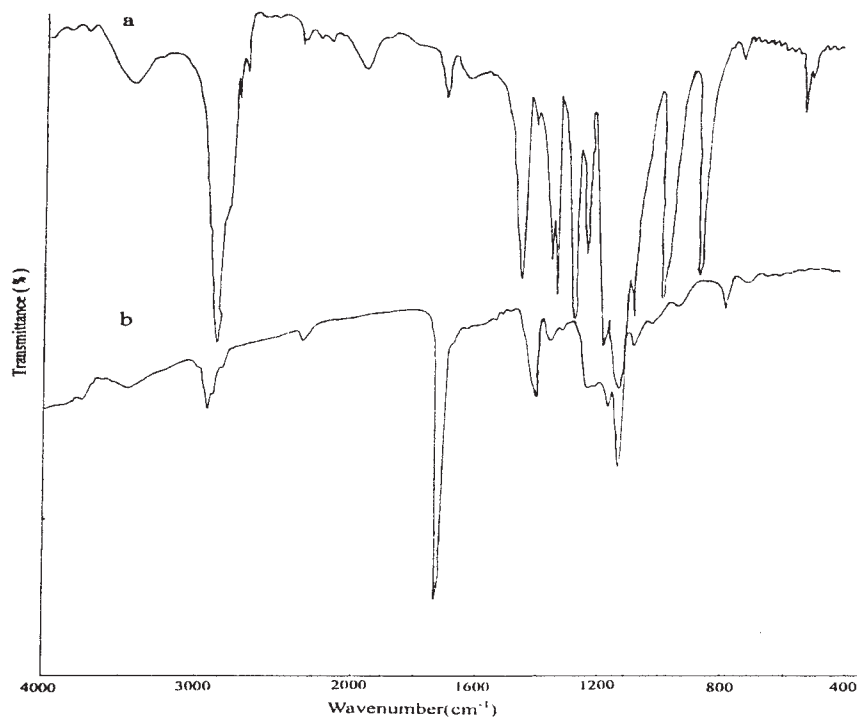


Figure 6 IR spectrum of PEG and a PMA-PEG-PMA block copolymer: (a) PEG, (b) PMA-PEG-PMA

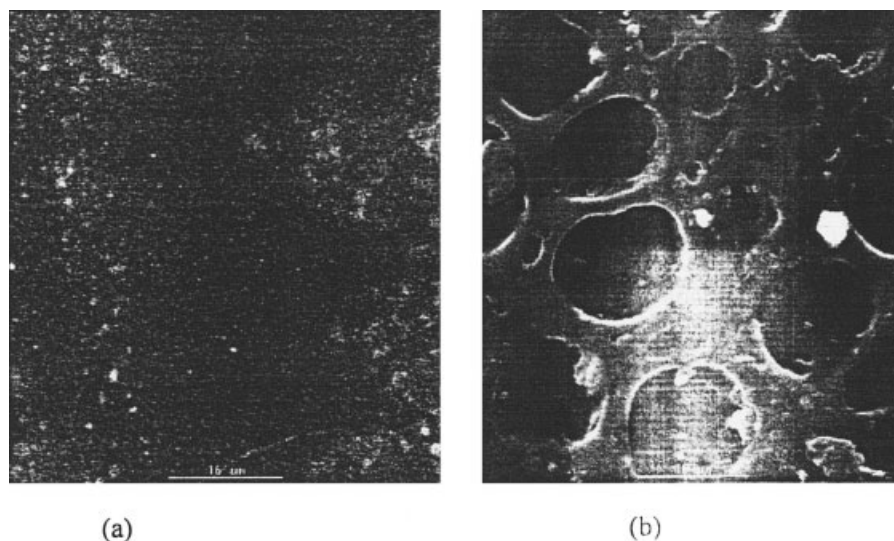
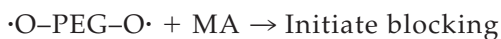
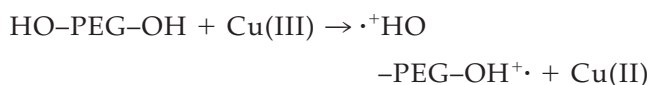


Figure 7 SEM micrographs of (a) PEG and (b) PMA-PEG-PMA.

A plausible initiation mechanism^{17,18} was proposed as follows:



Morphological studies (SEM)

The morphological characteristics of block copolymer and PEG were studied by SEM. As shown in Figure 7, it can be seen that the surface of the blocking polymer

has more holes than that of the PEG. It is ascribed to the different strengths of the molecular chain. Due to the effect of surface tension, the weaker molecular chain of PEG broke and holes were observed.

Thermal analysis

The thermal behavior of the block copolymer was examined by a study of its TGA thermograms. As shown in Figure 8, thermal decomposition of the sample took place in three main steps. The first stage may be due to the loss of adsorbed moisture. The second step between 310 and 410°C may correspond to the break of the PEG and PMA. The last step may be attributed to the carbonization.

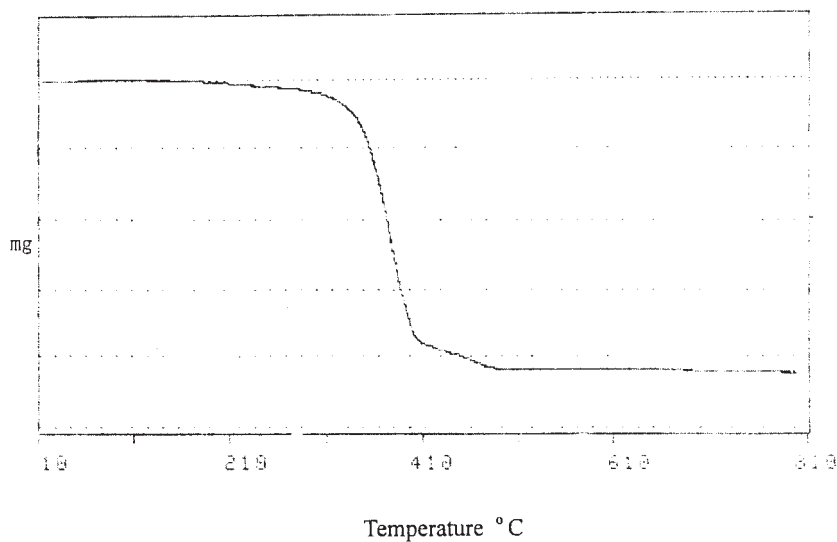


Figure 8 TGA thermograms of PEG PMA-PEG-PMA.

CONCLUSIONS

In this study, block copolymerization of MA with PEG was carried out with satisfactory results using DPC in an aqueous alkaline medium. The optimal conditions have been obtained and are as follows: temperature (318 K), concentration of [DPC] (3.159×10^{-5} mol/L), weight ratio of MA/PEG (6 : 1), and reaction time (4,800 s). The proof of blocking was obtained from ^1N -HMR and IR analysis. Based on the TGA and SEM results, it was found that the block copolymer was thermally stable and had more holes than the unblocked one, which may improve the hygroscopic power of the textile layer pastern of polyacrylate and broaden its range of application.

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