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Polyfunctional Initiation System for Preparation of Block Copolymer of Ethylene Oxide and Methyl Methacrylate by Sequential Initiation of Anion and Charge Transfer Complex and the Effect of Polymerization Conditions on the Copolymerization

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POLYFUNCTIONAL INITIATION SYSTEM FOR PREPARATION OF BLOCK COPOLYMER OF ETHYLENE OXIDE AND METHYL METHACRYLATE BY SEQUENTIAL INITIATION OF ANION AND CHARGE TRANSFER COMPLEX AND THE EFFECT OF POLYMERIZATION CONDITIONS ON THE COPOLYMERIZATION

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ABSTRACT

A block copolymer of hydrophilic and crystallinic polyethylene oxide and hydrophobic and noncrystallinic polymethyl methacrylate was prepared by sequential initiation of phenoxy anion and charge transfer complex using *p*-aminophenol as parents compound. The structure of the copolymer was characterized by GPC, IR, ^{1}H NMR, and DSC in detail. The propagating reaction of PMMA chain is dependent on the molecular weight and concentration of the first block PEO and the polarity of solvents, and the reasons for these phenomena are discussed.

INTRODUCTION

Recently, interest in the preparation of block copolymers comprising hydrophilic and hydrophobic chain segments has been stimulated by their successful application in the fields of biochemistry, biomedicine, and intelligent materials. The success can be attributed to their unique physicochemical properties and environmental sensitivity [1, 2]. The diblock copolymer of ethylene oxide (EO) and alkyl ethacrylate is an example of this kind of copolymer, which has been extensively studied by much research [3, 4]. It has proved to be effective in enhancing the miscibility of incompatible polymer, the stability of colloidal suspensions and micellar systems, and the performances of associative thickeners [5]. However, according to the classification of monomer reactivity [6], in sequential anionic polymerization only the living poly(alkyl methacrylate) anions can initiate the polymerization of EO; the converse of this sequence may not be true. Even if in the former case the side reactions between living poly(ethylene oxide) (PEO) and the alkyl ester group of poly(alkyl methacrylate) blocks due to the electrophilic attack of carbonyl to PEO's anion may occur, they would lead to the formation of inhomogeneous block copolymers [7].

Tomoi et al. [8] found that in some conditions when tetrahydrofuran (THF) was used as the solvent at low temperature, alkyl methacrylate could also be effectively polymerized by initiation with disodium alkoxides of poly(ethylene glycols) to obtain the corresponding block copolymer (PEO-*block*-PMMA). However, the synthesis of block copolymers through the addition of MMA to living PEO may involve at least two difficulties. First, the low reactivity of EO and the low solubility of PEO in THF require a higher polymerization temperature of at least 20°C, whereas most alkyl methacrylate anions are essentially unstable at that temperature [9], and transfer and termination reactions may take place. Second, transesterification reactions between PEO anions and MMA monomers may exist, resulting in grafted block copolymers [10].

In order to overcome the difficulties of preparation of the diblock copolymer of EO and methyl methacrylate (PEO-*block*-PMMA) by anion polymerization, a new initiation system with universal significance was designed by us. In it, anionic and charge transfer polymerizations were combined into one initiation system by protection and deprotection of functional groups. A well-defined PEO-*block*-PMMA is the result.

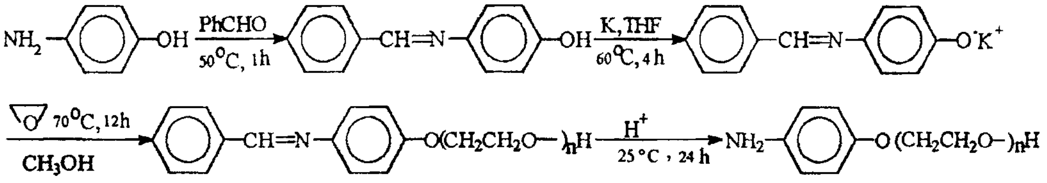
EXPERIMENTAL

Materials

Commercial MMA was purified by the usual method and distilled under reduced pressure [11]. EO was dried with calcium hydride, then distilled under N_2 atmosphere before use. All other solvents were purified by conventional drying and distillation procedures. *p*-Aminophenol (from Tao Yuan Reagent Factory, WuJian county, ShuZhou City, China) was recrystallized twice with alcohol, then water, giving crystals with a dark yellow color in a percent recovery of 83.2, mp 187–188°C. Benzophenone (BP) (Shanghai First Chemical Reagent Factory, CP) was also purified by recrystallization with alcohol.

Preparation of PEO with Aniline End Group (PEO_a)

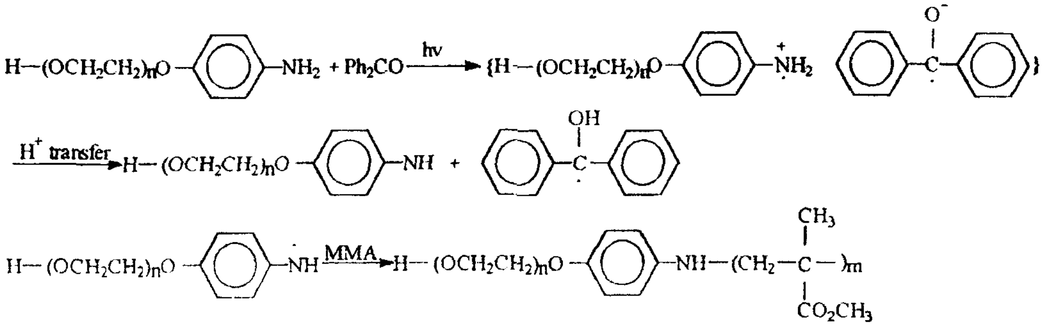
Anionic polymerization of EO using protected *p*-aminophenol sodium as initiator has been reported in a previous paper [12]. The process can be described as follows:



No chain cleavage of PEO prepolymer with an aniline end group was found by GPC check during the entire anionic polymerization.

Preparation of PEO-*block*-PMMA by Charge Transfer Polymerization

Charge transfer polymerization (CTP) of MMA by initiation of CTC consisted of PEO with an aniline end group and BP under UV irradiation was performed according to the following:



In a 100-mL ampule containing 1.44 g (1.2×10^{-4} mol) of PEO prepolymer with the aniline end group, 0.022 g (1.2×10^{-4} mol) of BP in 10 mL benzene and 5 mL MMA were added, then the ampule was linked to the vacuum system for degassing. After three cycles of freeze-pump-thaw at 77 K, the ampule was sealed and irradiated with a 300-W high-pressure mercury lamp (model DDZ-300, manufactured by Shanghai Ya Ming Lamp Factory) for 24 hours at a constant 25°C. Cupric sulfate aqueous solution was used as a photofilter to obtain 365 nm monochromatic light. The block copolymer was precipitated in *n*-hexane and extracted with cold water to remove the PEO prepolymer. The weight of purified and dried copolymer is about 0.76 g.

Measurements

The ^{1}H-NMR spectrum was recorded on a Varian XL-300 NMR spectrometer with TMS as the internal standard and $CDCl_3$ as the solvent. The IR spectrum was obtained on a Necolet Magna-550 IR spectrometer. The molecular weight and molecular weight distribution of the copolymer were derived with a Shimadzu LC-3A gel permeation chromatography (GPC) with a microcomputer using both UV and refractive index detectors. Polystyrene standards were used for calibration, and the weight- and number-average molecular weights were accordingly calculated. The influence of the concentration and molecular weight of PEO_a on the CTP was determined by an improved dilatometer which was connected to the vacuum system to remove the oxygen in the reactor at 77 K.

RESULTS AND DISCUSSION

Characterization of Block Copolymer

Figure 1 shows the IR spectrum of purified PEO-*block*-PMMA. The strong band at 1149 cm^{-1} (C—O—C) attributed to PEO and the band at 1728 cm^{-1} (C=O) attributed to PMMA strongly suggest PEO-*block*-PMMA. From the ^{1}H-NMR spectrum of the sample shown in Fig. 2, typical resonance signals of protons in PEO and PMMA chain segments appeared, such as 3.64 ($-CH_2CH_2O$) for PEO, 0.84 (syndiotactic) and 1.02 (heterotactic) $(CH_3-\overset{|}{\underset{|}{C}}-)$, 1.81 ($-CH_2-$), and 3.60 ($-O-CH_3$) for PMMA.

The formation of PEO-*block*-PMMA could also be confirmed by GPC measurements. Figure 3 gives data on the molecular weight and molecular weight distribution (MWD) of the sample. Curve A denoted the PEO prepolymer; its molecular

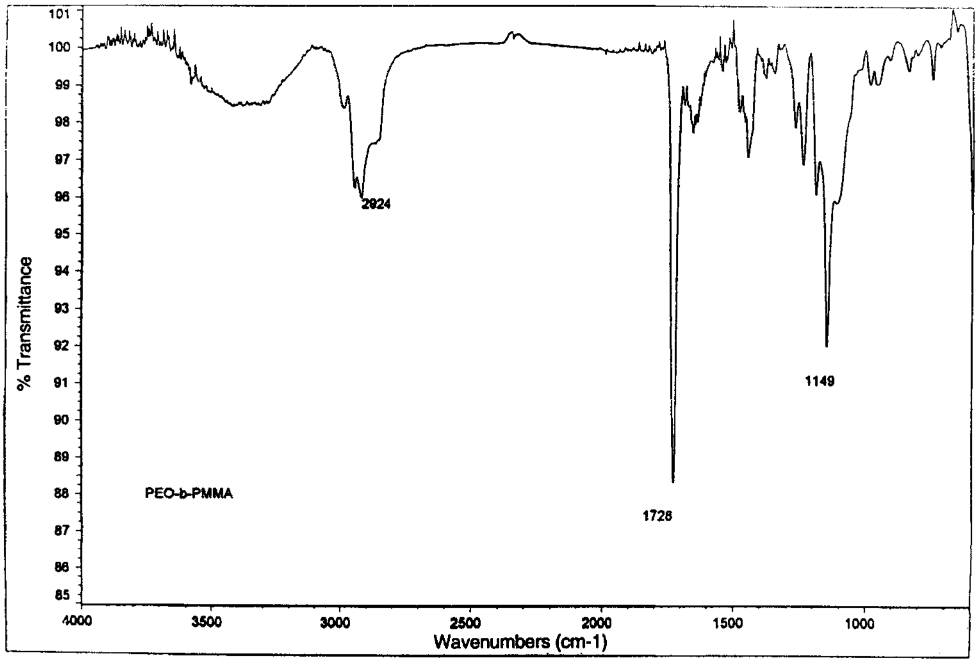


FIG. 1. IR spectrum of PEO-*block*-PMMA.

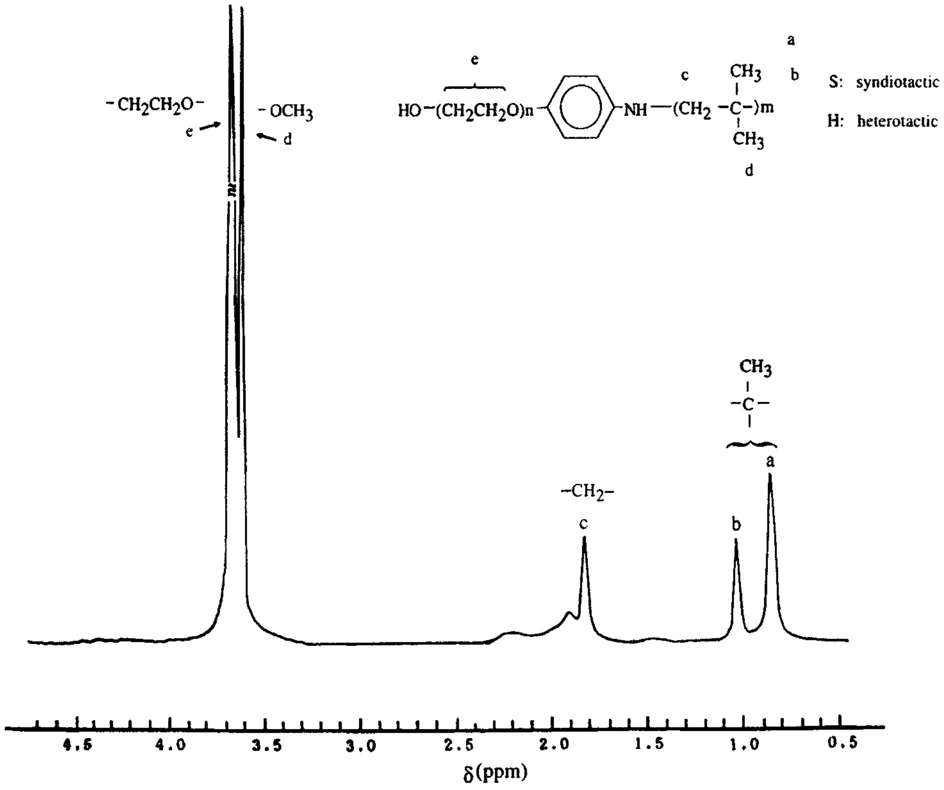


FIG. 2. ^{1}H-NMR spectrum of PEO-*block*-PMMA.

weight is about 11,000 and the MWD is 1.05. In Curve B there is also only one peak with a small retention volume; its molecular weight is about 44,000 and the MWD is 1.40.

Effect of the Solvent Polarity on the CTP of MMA

It is well known that when a binary initiation system composed of BP and aromatic amine is irradiated by 365 nm light, BP molecules in the ground state will absorb the photon first and be in the excited singlet state. They then decay to the excited triplet by intersystem crossing. In this state they combine with an aromatic amine molecule to form an exciplex, from which an aromatic amine radical and diphenyl methanol radical are produced through the transfer of a proton from the aromatic amine to BP. The diphenyl ethanol radical is too stable to initiate the polymerization. Therefore, the polymer was formed only by initiation by the imino radical [13, 14].

It was found that solvent polarity can exert a great effect on the CTP of MMA. Table 1 presents some data of the composition, molecular weight, and molecular weight distribution of the copolymer and MMA conversion when the block copolymerization was carried out in different solvents. The conversion of

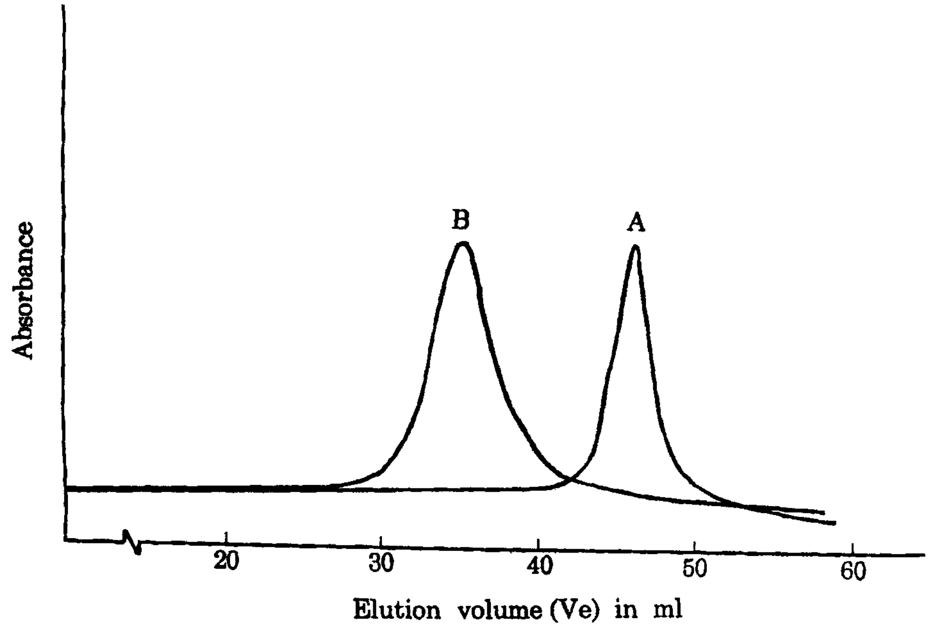


FIG. 3. GPC measurement of PEO-*block*-PMMA. Peak A is PEO, and Peak B is PEO-*block*-PMMA.

MMA in benzene was higher than in acetonitrile. In contrast, the MMA content in copolymer composition is higher in the latter than in the former.

How do we explain this phenomenon? According to the initiation mechanism of a binary system composed of BP and an aromatic amine [15], we suggest that when the excited triplet BP combines with PEO_a, an exciplex is formed first via

TABLE 1. Effect of the Polarity of the Solvent on the Block Copolymerization[a]

Sample	Concentration of PEO_a ($\times 10^3$ mol/L)	Content of PMMA in copolymer, mol%		MW of PMMA ($\times 10^4$)	Conversion of PMMA, %	$\bar{M}_w/\bar{M}_n$
		Conversion	GPC			
Benzene:						
1	9.56	18.62	19.35	6,000	5.51	1.24
2	6.21	50.43	63.77	44,000	7.84	1.40
Acetonitrile:						
1	9.56	21.03	22.36	7,200	4.87	1.28
2	6.21	59.22	66.67	50,000	6.99	1.43

[a] MW of PEO_a: 11,000. $\bar{M}_w/\bar{M}_n$: 1.05. Concentration ratio of BP and PEO_a: 1:1 (mol/mol). Polymerization temperature: 25°C. Time: 24 hours. MMA: 5 mL. Benzene or acetonitrile: 10 mL.

mono-electron transfer, then the different reaction routes may be undergone, dependent on the polarity of the solvents. In a nonpolar solvent such as benzene, the aromatic amine radical and diphenyl methanol radical are formed via proton transfer from the cation radical of the aromatic amine to the BP anion radical, then the imino radical initiates the polymerization of MMA. However in a strong polar solvent such as acetonitrile, the ion radical pairs consisting of BP and PEO$_a$ may be solvated, the tightly bound ion radical pairs are turned into loose pairs, and thus any proton transfer between them might be very difficult to carry out because the increase of the distance between them leads to a decrease of the radical concentration, and that is the direct cause for the decrease of MMA conversion in a strong polar solvent. Nevertheless, the molecular weight of PMMA increased in the latter conditions due to the inverse dependence of the kinetic chain length on the radical concentration in radical polymerization.

Effect of the Concentration and Molecular Weight of PEO$_a$ on the Block Copolymerization

Figure 4 shows the effect of the concentrations of *p*-aminophenol and PEO$_a$ (MW: 11,000) on the polymerization rate of MMA. In the case of acetonitrile as solvent, the polymerization rate increased with an increase in the concentration of *p*-aminophenol ($< 10^{-2}$ mol/L) when the concentration of BP and MMA was kept constant. A nice linear relationship between them was found, and $R_p \propto$ [NH$_2$—⌬—OH]$^{0.41}$ could be derived from the slope of the straight line. However, in the same conditions when PEO$_a$'s concentration was less than 6.5×10^{-3} mol/L, a linear

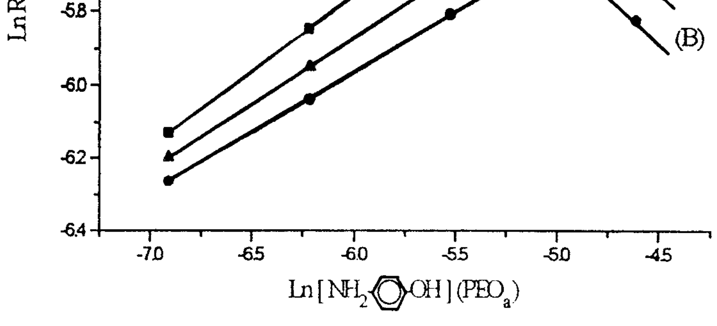


FIG. 4. Effect of concentrations of *p*-aminophenol (A) and PEO$_a$ (B,C) on the polymerization rate (R_p). For Curves A and B, acetonitrile was the solvent; for Curve C, benzene was the solvent. Molecular weight of PEO$_a$: 11,000.

relationship was also obtained with $R_p \propto [\mathrm{PEO_a}]^{0.32}$; when the concentration of $\mathrm{PEO_a}$ was greater than 6.5×10^{-3} mol/L, R_p started to decrease and the maximum R_p appeared. This may be attribute to the following two causes: 1) a part of the amino groups in the solvent are enveloped due to the entanglement of $\mathrm{PEO_a}$ chains, so the efficient concentration of amino groups decreases. As is well known, the entanglement density of polymer chains is dependent on the molecular weight and concentration of the macromolecules and on the polarity of the solvent. When acetonitrile, which is good solvent for PEO and PMMA, is used, the entanglement density of $\mathrm{PEO_a}$ in dilute solution is rather small, and the amino end groups are fully laid bare. In this case, the behavior of $\mathrm{PEO_a}$ in the polymerization of MMA is very similar to that with a small aromatic amine. After that, the entanglement density increased gradually with an increase of the concentration of $\mathrm{PEO_a}$. However when the concentration of $\mathrm{PEO_a}$ approaches 6.5×10^{-3} mol/L, R_p starts to decrease, which means that in this case the amino end groups are really covered. When benzene, which is not a good solvent for either PEO or PMMA, is used in the same conditions, the critical concentration of $\mathrm{PEO_a}$, which affects the R_p, is lower than that of the case of acetonitrile, as Fig. 4(C) shows. Its value is about 6.3×10^{-3} mol/L.

2) When the concentration of $\mathrm{PEO_a}$ is greater than the critical one, hydrogen bonds of intra- or intermacromolecules may be formed due to the interaction between the oxygen atoms of $\mathrm{PEO_a}$ and the hydrogen atoms of the amino end groups, and the electron and proton transfers from $\mathrm{PEO_a}$ to BP may be difficult to carry out, so the concentration of the radicals decreases, leading to a decrease of R_p. This phenomenon was found in both the good and poor solvents.

Figure 5 describes the effect of molecular weight on R_p. With the premise of keeping the same polymerization conditions as when $\mathrm{PEO_a}$ with a molecular weight

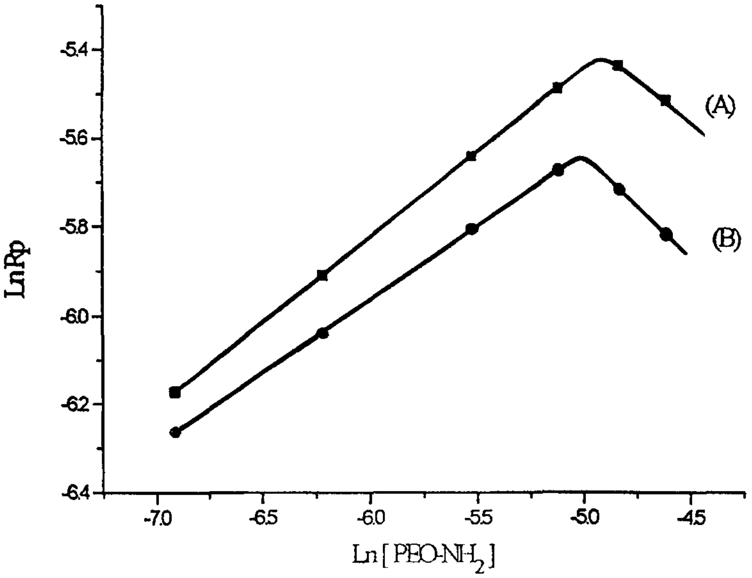


FIG. 5. Dependence of R_p on the molecular weight of $\mathrm{PEO_a}$. A = 5,000; B = 11,000.

of 5000 was used, with $R_p \propto [PEO_a]^{0.38}$, the concentration factor of PEO_a is greater than that of the case of molecular weight of 11,000, approaches gradually to 0.41 of small *p*-aminophenol, and the critical concentration of PEO_a increased also to 7.66×10^{-3} mol/L. It could also be explained by the entanglement of macromolecule chain: when the molecular weight of PEO_a decreases, the amount of macromolecule chain necessary to have the same entanglement density as its high molecular weight counterpart should increase, so the critical concentration is raised, and the factor increases too.

The critical concentration of macromolecular entanglement which affected the block copolymerization was obtained by kinetic measurement. It could also be derived by fluorescence measurement of the exciplex composed of PEO_a, the donor, and the anthrophinone acceptor. The results of both measurements are identical and will be published in another article.

CONCLUSION

A well-defined block copolymer composed of hydrophilic PEO and hydrophobic PMMA was successfully prepared by a combination of anion and charge transfer polymerization mechanisms using *p*-aminophenol as the parent compound. Variation of the polymerization mechanism was achieved by protection and deprotection of the functional groups. In a polar solvent the radical ion pairs formed by electron transfer from PEO_a to BP were solvated, the further proton transfer was difficult to carry out, so the block copolymerization of MMA was affected. The formation of a second block chain of MMA is dependent on the molecular weight and concentration of PEO_a.

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