

A Moderately Water-Soluble Azo Initiator for Emulsion Polymerizations

INTRODUCTION

A variety of different free radical initiators has been used in emulsion polymerization, particularly water-soluble salts such as ammonium and potassium persulfate. Non-ionic oil-soluble initiators such as 2,2'-azobisisobutyronitrile (AIBN) have also been employed in emulsion polymerization, for example, in the work of Il'menev et al.¹ Although the classical Smith-Ewart model of emulsion polymerization² has until recently been thought to apply only to systems with water-soluble initiators. Capek et al.³ found that it is possible to apply the Smith-Ewart model to AIBN-initiated polymerizations. They found that the rates of polymerization and initiation were higher and the molecular masses lower with a water-soluble initiator than with an oil-soluble initiator.

The use of nonionic water-soluble initiators offers some potential advantages over conventional persulfates or redox systems. This is particularly true when the presence of ionic fragments derived from the initiator is undesirable, either in the latex serum or on the surfaces of the polymer particles. Such species are known to affect the colloidal stability of the latex and can also influence the morphology of particles produced in sequential polymerizations of different polymers, as in so-called core-shell particles.⁴ The use of persulfate salts also results in drastic pH drops during the course of an emulsion polymerization. This often necessitates the addition of a buffer, which contributes to the ionic strength of the serum and instability of the polymer emulsion.

Herein, we describe the use of the nonionic azo initiator *N,N'*-dimethyldiazenedicarboxamide as an initiator for the emulsion polymerization of methyl methacrylate. This material has more water solubility than does AIBN or other common azo initiators at temperatures near 90°C. It may therefore be a more attractive source of radicals in the aqueous phase when ionic initiators cannot be used, for the reasons given.

EXPERIMENTAL

Preparation of *N,N'*-Dimethyldiazenedicarboxamide

1. Methylisocyanate (Aldrich) (6.28 g) was dissolved in 150 mL dioxane. To this, 1.80 g hydrazine dissolved in 50 mL dioxane was added dropwise with

stirring. Immediate formation of a white precipitate was noted. After stirring for 1 h, the precipitate (MeNHCONHNHCONHMe) was recovered in 76.5% yield.

2. MeNHCONHNHCONHMe (0.29 g) was dispersed in 100 mL CH₂Cl₂. *N*-bromosuccinimide (Aldrich) (0.36 g) and 0.16 pyridine (Baker) was added to the mixture with stirring. The mixture changed from white to brilliant orange. Stirring was continued overnight, and the orange product was recovered in 89% yield.

The final product (CH₃NHCON = NCONHCH₃) was characterized by ¹H-NMR spectroscopy. A singlet was observed at 2.95 ppm.

Emulsion Polymerizations

MMA polymerizations were carried out in both batch and semibatch polymerization modes. Reagent-grade methyl methacrylate was obtained from Aldrich and commercial grade sodium dodecylbenzenesulfonate surfactant from Alcolac. Reagent-grade water was obtained from a Waters Milli-Q purification system. Polymerizations were carried out in a 1 L glass kettle reactor maintained in a thermostated water bath and equipped with a stirrer, condenser, and, for semibatch polymerizations, a monomer pump. Stirring was set at 200 rpm. A nitrogen blanket was maintained during the polymerizations. The polymerization temperature was 90°C.

A typical recipe for a semibatch polymerization is as follows:

	Ingredient	Amount (g)
Reactor charge:	(a) water	150
	(b) dodecylbenzene sulfonate	1.0
Preemulsified feed:	(a) water	100
	(b) dodecylbenzene sulfonate	0.7
	(c) methyl methacrylate	90
	(d) initiator	0.7

The preemulsified feed was added to the reactor at a rate of 1.7 mL/min. In the batch polymerizations, all the ingredients except the initiator were added to the reactor and warmed to the reaction temperature, whereupon the initiator was added to the reactor.

Initiator Half-life

The half-life of *N,N'*-dimethyldiazenedicarboxamide was measured at 80 and 90°C. Decomposition of the initiator in dilute solutions maintained at these temperatures was followed by UV spectrophotometry using a Perkin-Elmer λ -5 UV-visible spectrophotometer.

Latex Particle-size Determination

A Joyce-Loebl disc centrifuge was used for latex particle-size analysis. Water was used as the spin fluid with added methanol to produce a density gradient. Data were digitally recorded and analyzed.

Molecular Weight Determination

Polymer molecular weights were determined by size-exclusion chromatography in THF at room temperature using a differential refractive index detector and universal calibration with anionic polystyrene standards.

RESULTS AND DISCUSSION

Emulsion polymerization of methyl methacrylate using *N,N'*-dimethyldiazenedicarboxamide was achieved with 85–90% conversion of monomer in both batch and semi-batch polymerization modes with no coagulation noted. The solubility of the initiator in water at room temperature was found to be 0.06 g/mL (cf. 0.036 g/mL for AIBN¹). The initiator was significantly soluble in water at the reaction temperature with concomitant decomposition. The half-life of the initiator was found to be 1.2 h at 80°C and 34 min at 90°C.

Particle diameters with our recipes were typically in the range 120–130 nm with a polydispersity of 1.05. Representative molecular weight data are $M_w = 1.03 \times 10^6$ g/mol and $M_w/M_n = 2.5$.

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REFERENCES

1. P. Y. Il'menev, G. I. Litvinenko, V. A. Kaminskii, and I. A. Gritskova, *Pol. Sci. USSR*, **30**, 826 (1988).
2. W. V. Smith and R. H. Ewart, *J. Chem. Phys.*, **16**, 592 (1948).
3. I. Capek, J. Barton, and A. Karpatyova, *Makromol. Chem.*, **188**, 703 (1987).
4. I. Cho and K.-W. Lee, *J. Appl. Pol. Sci.*, **30**, 1903 (1985).

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