Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Seymour, Raymond B. and Stahl, G. Allan(1977) 'Preparation of Block Copolymers of Vinyl Acetate in. Viscous Poor Solvents', Journal of Macromolecular Science, Part A, 11: 1, 53 — 64

To link to this Article: DOI: 10.1080/00222337708061251

URL: http://dx.doi.org/10.1080/00222337708061251

J. MACROMOL. SCI.–CHEM., A11(1), pp. 53-64 (1977)

Preparation of Block Copolymers of Vinyl Acetate in Viscous Poor Solvents

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ABSTRACT

Stable macroradicals of poly(vinyl acetate) were produced by heating vinyl acetate (VAC) and 2% tert-butyl peroxypivalate at 50° C for 96 hr in silicone oil. Block copolymers were produced from these macroradicals by adding a second vinyl monomer and heating at 50° C for an additional 72 hr. The formation of these macroradicals was monitored by yield, dilatometric rate data, and scanning electron micrographs. Poly(vinyl acetate-b-methyl methacrylate), poly(vinyl acetate-b-acrylic acid), poly(vinyl acetate-b-acrylonitrile), poly(vinyl acetate-b-vinylpyrrolidone), poly(vinyl acetate-b-styrene), and poly(vinyl acetate-b-methyl methacrylate-b-styrene) were characterized by yield, selective precipitation, pyrolysis gas chromatograph, and differential scanning calorimetry (DSC).

INTRODUCTION

Block copolymers of VAC from polymers containing peroxy [1] or other reactive end groups [2] by γ-irradiation [3-6] and mechanochemical techniques [7, 8], and by the addition of VAC to occluded macroradicals [9-11]. It has been shown previously that a difference in solubility parameters between the solvent and polymer of at least 1.8 Hildebrand units was required for the formation of stable occluded macroradicals [12].

It has also been shown that stable macroradicals suitable for the preparation of block copolymers can be produced in viscous good solvents as a result of the gel effect [13] and also in viscous poor solvents [11]. Silicone oils were used in the investigation in order to investigate the preparation of block copolymers of VAC in viscous poor solvents.

EXPERIMENTAL

All vinyl monomers were purified by distillation under reduced pressure. VAC was dried over anhydrous Na_2SO_4 before double distillation. Macroradicals of VAC were prepared by heating 1 g of VAC for 96 hr in 19 g of solvent at 50° C in the presence of 0.06g of tert-butyl peroxypivalate (t-BPP) (Lupersol 11, Lucidol Div. Penwalt Corp., 75% solution in mineral spirits, half-life 12 hr at 50° C, used as received). All samples were deoxygenated with zero-grade argon prior to initiation. Block copolymers were prepared by adding 1 g of vinyl monomer to the VAC macroradicals and heating these systems at 50° C for 96 hr.

Dow-Corning, 200 fluid (polydimethylsiloxane) in 50, 200, and 500 cS viscosities were used without further purification as the polymerization solvent.

Relative rates of VAC macroradical formation and block copolymerization were monitored by a previously described, precision dilatometer [14]. The dilatometer was charged with 2 g VAC, 50 ml solvent, and 0.12 g t-BPP at 50° C.

Electron microscopy samples were coated with Au/Po with a Technics Hummer and micrographs made on a Cambridge Stereoscan, Model S410.

Pyrolysis gas chromatographs (PGC) were obtained on a model A100C Aerograph (Wilkens) equipped with a Servo-Ritter II recorder (Texas Instruments), and a column packed with acid-washed Chromosorb W (Johns-Manville Corp.) and 20% SE-20 (General Electric).

Differential scanning calorimetry was performed on a DuPont Model 990 DSC thermal analyzer.

DISCUSSION

A proper solvent, in a study of VA polymerization, must demonstrate a low rate of radical chain transfer. In the previous study, tert-butanol and cyclohexane were selected for this reason. In this paper polydimethylsiloxane (silicone oil) was selected because it is commercially available in a wide range of viscosities, differs in solubility parameter from PVA by at least 2.8 H, and demonstrates low radical chain-transfer activity.

As shown in Fig. 1, benzene retards the polymerization of VAC, presumably because of radical chain transfer. The rate of polymerization is faster in low viscosity (50 cS) silicone oil, and the fastest in the most viscous (500 cS) silicone oil.

As shown in Fig. 2, the rate of formation of block copolymers of methyl methacrylate (MMA), as shown by yield data, was fastest in the high viscosity silicone oil.

As shown by the scanning electron micrograph (SEM), with a magnification of 1725× (Fig. 3), spheres of PVAC with a cross section of 10 μm were obtained in hexane, which is a nonviscous poor solvent for PVAC. Other particles obtained under these experimental conditions had cross sections in the 4.0-10.0 μm range.

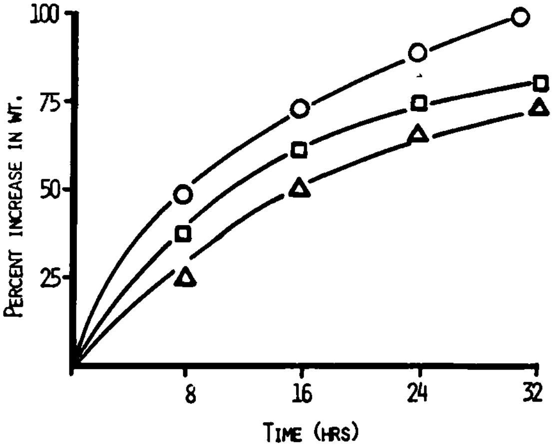

FIG. 1. Rate of polymerization of VAC: (●) in benzene; and in silicone oils of different viscosities: (△) 50 cS, (□) 200 cS, (○) 500 cS.

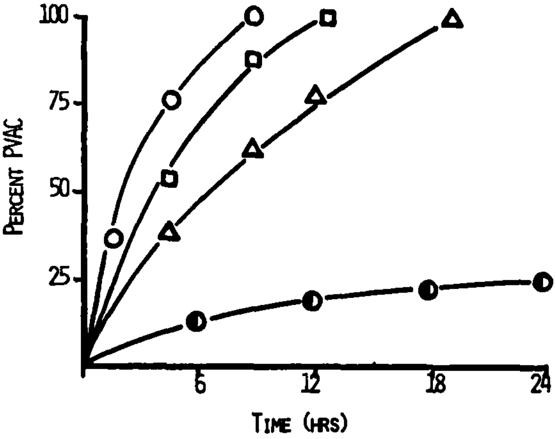

FIG. 2. Rate of addition of MMA to VAC macroradicals in silicone oil of different viscosities: (△) 50 cS; (□) 200 cS; (○) 500 cS.

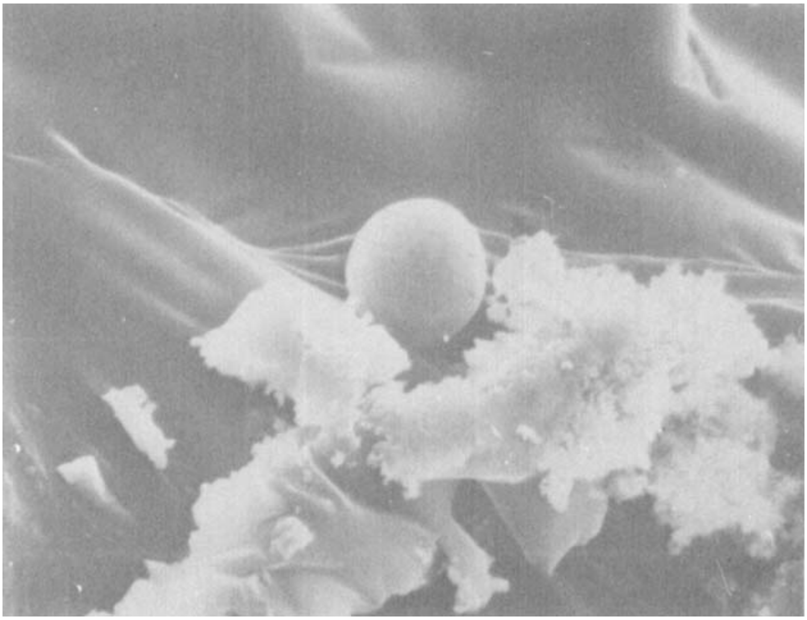

FIG. 3. SEM micrograph of PVAC produced in hexane at 50° C. 1725×.

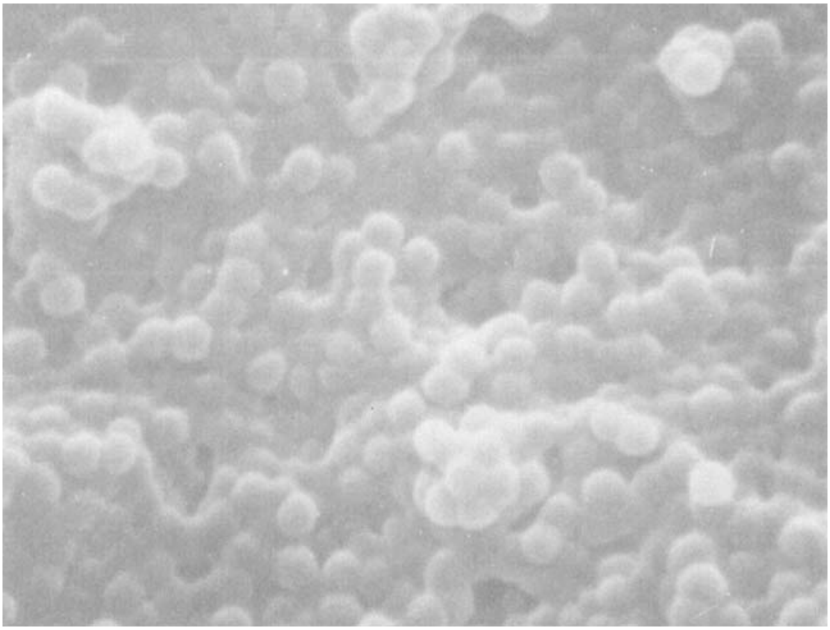

FIG. 4. SEM micrograph of PVAC produced in 500 cS silicone oil at 50° C. 21,000×.

As shown by the SEM with a magnification of 21,000× (Fig. 4), relatively uniform smaller spheres with cross sections of 230 ± 10 nm were produced in 500 cS silicone oil which was a poorer and more viscous solvent than hexane. That the reduction in particle size is independent of viscosity is demonstrated by the relative uniform particle size of 230 ± 10 nm cross section shown by SEM at a magnification of 55000× (Fig. 5). This observation is in accord with the concept that the size of the original precipitated macroradical is related to the difference in solubility parameter of the macroradical and solvent.

As shown in Table 1, good yields of product (91.7-100%) containing relatively large proportions of block copolymers (66.7-81.4%) were obtained when MMA, acrylonitrile (AN), vinylpyrrolidone (VP), and acrylic acid (AA) were heated with an equal weight of VAC macroradical. The difference between the solubility parameter of VAC macroradicals and these monomers was as follows: VP (2.6 H),

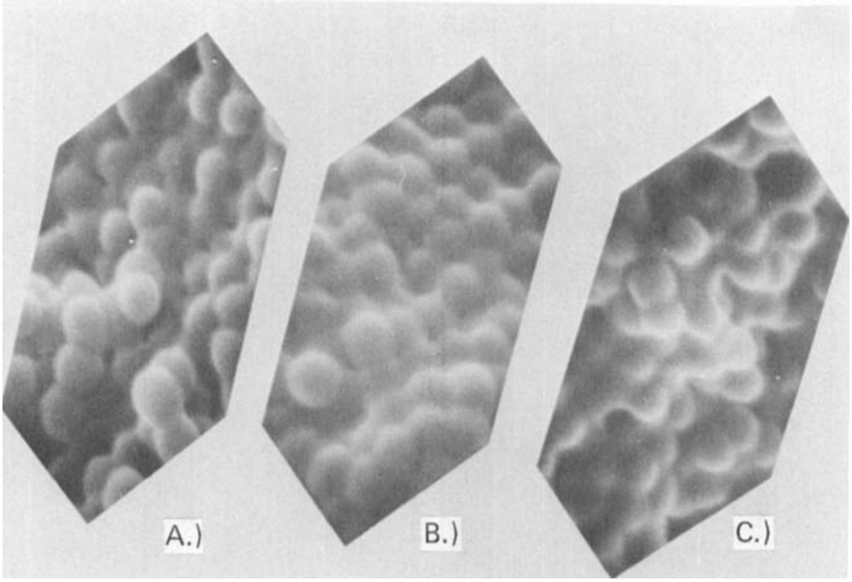

FIG. 5. SEM micrograph of PVAC produced in silicone oil of different viscosities: (A) 50 cS; (B) 200 cS; (C) 500 cS. 55000×.

TABLE 1. Composition of Polymeric Products Obtained by Heating Equal Weights of Vinyl Monomers with VAC Macroradicals in 500 cS Silicone Oil at 50° C

Monomer X	Homo-polymer PVAC (%)	Homo-polymer PX (%)	Block copolymer P(VAC-O-X) (%)	Total yield (%)
S	51.3	37.0	11.6	81.1
VP	24.0	9.4	66.7	95.0
AN	20.3	2.7	76.8	100
AA	15.8	3.6	80.6	91.7
MMA	16.3	2.3	81.4	100

AA (2.6 H), AN (1.1 H) and MMA (0.64 H). The lower yield of styrene (S) block copolymer (11.6%) is attributable to high chain transfer of VAC with S (Table 1).

Good yields 86.8% of block copolymers of VAC and S were prepared by adding S to VAC(90-b-MMA(10) macroradicals. This polymeric product contained 20.6 and 7.3% of PVAC and PS, respectively, and 72.1% of P(VAC-b-MMA-B-S).

The rate of formation of VAC and VAC-b-MMA macroradicals and P(VAC-b-MMA-B-S) in silicone oil (500 cS) at 50°C is shown in Fig. 6.

CHARACTERIZATION

The block copolymers obtained from VAC macroradicals were purified by precipitation with selected solvents. The mixtures of homopolymers and block copolymers were first dissolved and then fractionally precipitated by the gradual addition of a poor solvent.

P(VAC-b-MMA) was purified by first dissolving in benzene. PMMA was precipitated by the addition of 1.6 parts of methanol

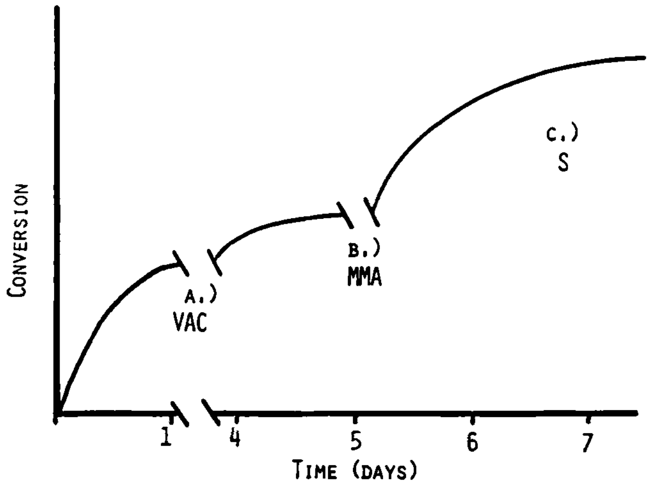

FIG. 6. Rates of polymerization: (A) VAC; (B) addition of MMA, and (C) addition of S in 500 cS silicone oil at 50° C.

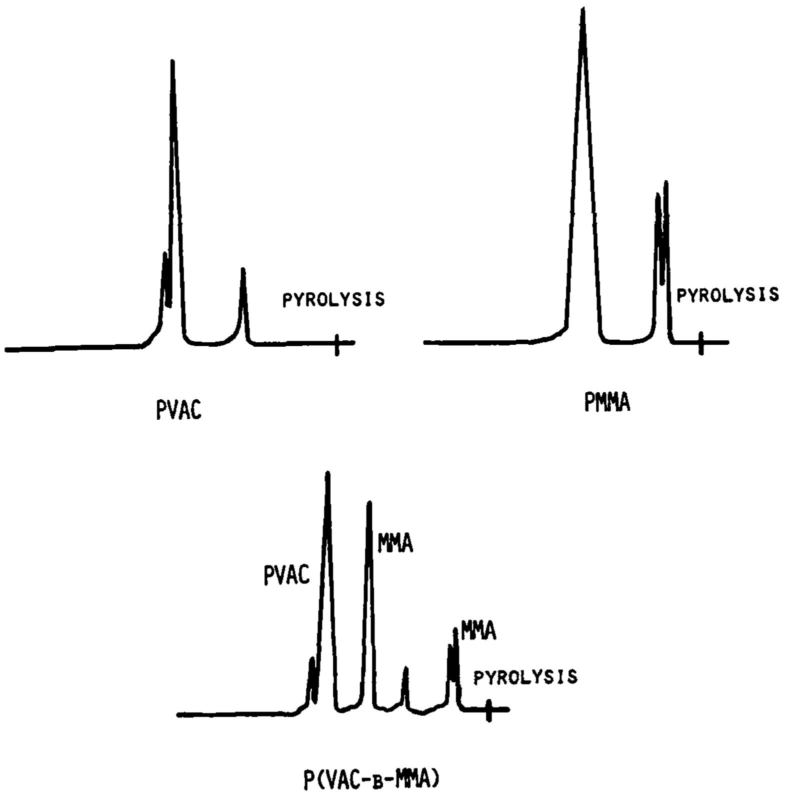

FIG. 7. Typical GC pyrograms of PVAC, PMMA, and P(VAC-b-MMA).

(containing 1% calcium chloride as a coagulation aid) to 1 part benzene. The block copolymer was removed by the addition of 2.5 parts methanol (plus $CaCl_2$). The remaining PVAC was precipitated by adding petroleum ether.

P(VAC-b-AA) was purified by dissolving in acetone, followed by the addition of 0.7 parts petroleum ether to precipitate the PAA. The block copolymer was precipitated by adding 1.5 parts petroleum ether.

P(VAC-b-VP) was also purified by the acetone-petroleum ether technique. PAA was removed by the addition of 0.4 parts petroleum

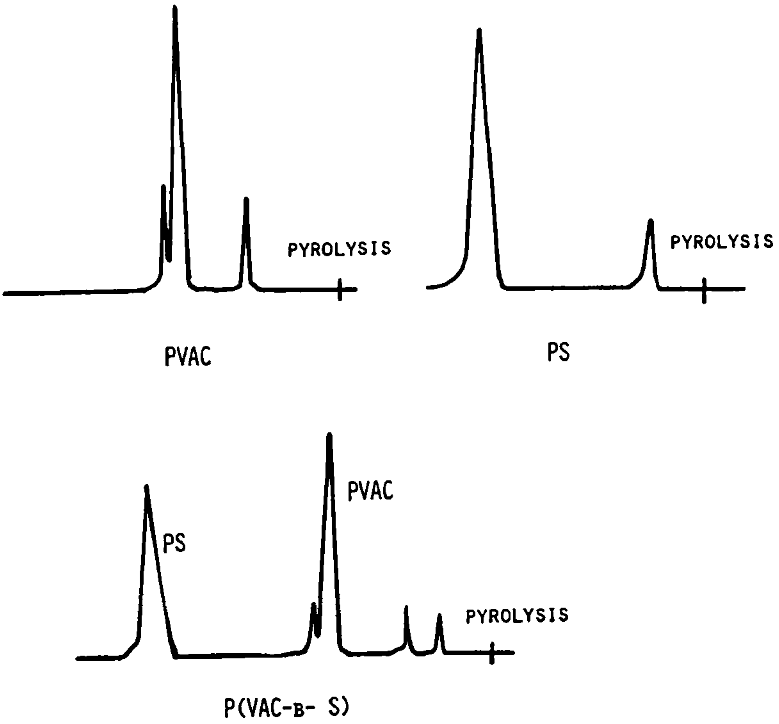

FIG. 8. Typical GC pyrograms of PVAC, PS, and P(VAC-b-S).

ether, while the block copolymer precipitated when more than 1.5 parts of petroleum ether was added.

P(VAC-b-AN) was purified by benzene extraction in a soxhlet extractor. The supernate was fractionally precipitated by the addition of 0.2 parts petroleum ether which precipitated the block copolymer. PVA was precipitated by the addition of more than 0.6 parts petroleum ether.

P(VAC-b-S) was purified by precipitation from a benzene solution. The addition of 0.6 parts petroleum ether removed the PVAC, while the block copolymer was precipitated by the addition of 1.0 part of petroleum ether.

Yields were determined on the solvent-purified samples. The latter were characterized by pyrolysis gas chromatography. Typical gas chromatograms are shown in Figs. 7 and 8. DSC thermograms

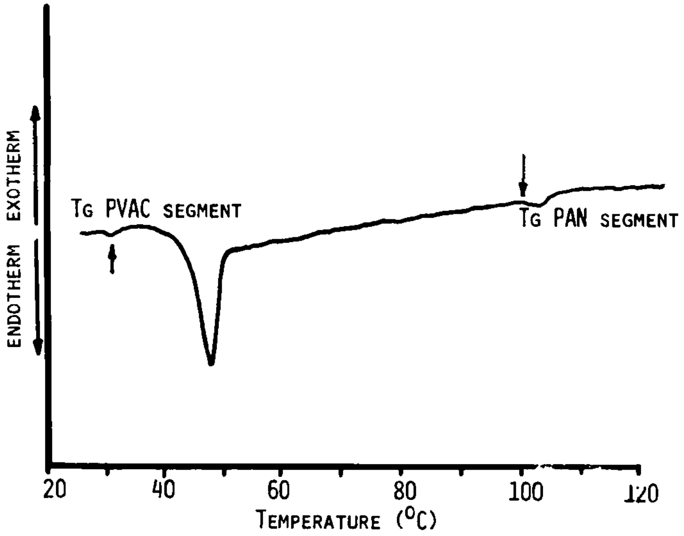

FIG. 9. Typical DSC thermogram of P(VAC-b-AN).

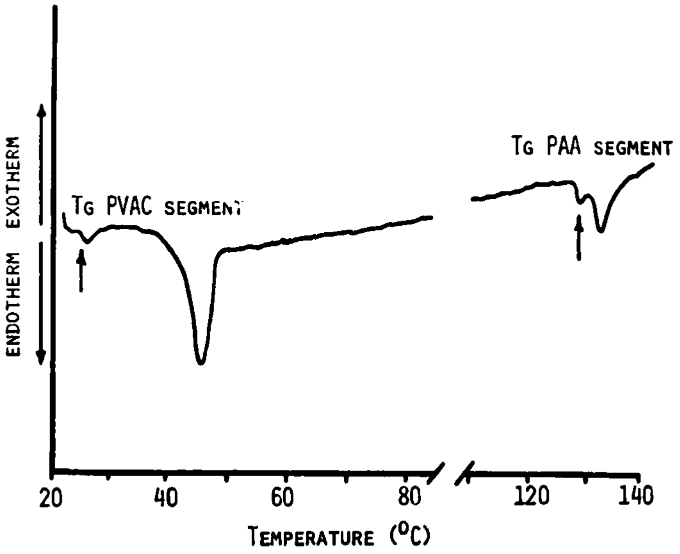

FIG. 10. Typical DSC thermogram of P(VAC-b-AA).

of these samples showed the characteristic glass transitions for each constituent of the block. Typical thermograms are shown in Figs. 9 and 10.

CONCLUSIONS

Good yields of block copolymers of VAC and MMA, AA, AN, VP, and S were obtained by adding the respective monomers to VAC macroradicals in silicone oil, a viscous poor solvent. The effect of solvent solubility parameter and viscosity were investigated by precision dilatometry and SEM. It was found that VAC macroradicals polymerized in spheres with a cross section of approximately 230 nm. The size of these spheres was independent of the viscosity but appears to be related to the solubility parameter of the poor solvent. The rate of polymerization was fastest in the more viscous, 500 cS silicone oil.

The yield of block copolymer was greatest in the viscous poor solvent. The solvent-extracted block copolymers were characterized by PGC and DSC.

ACKNOWLEDGEMENTS

The authors wish to thank Messrs. Ray Clark and Dave Feurbacher of Dresser Industries, Inc., Houston, Texas for the DSC thermograms. This investigation was supported in part by the Robert A. Welch Foundation and the ACS Petroleum Research Fund.

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Accepted by editor April 3, 1976
Received for publication May 5, 1976