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OFFICE OF NAVAL RESEARCH

CONTRACT N00014-94-1-0101

R&T Code 31321075

Technical Report No. 22

RADICAL POLYMERIZATION OF VINYL ACETATE IN THE PRESENCE OF TRIALKYL PHOSPHITES

by

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Published

in the

ACS Polym. Preprints, 35(1), 466 (1994)

Carnegie Mellon University
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4400 Fifth Avenue
Pittsburgh, PA 15213

DTIC QUALITY INSPECTED 2

June 30, 1994

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94-20043

94 6 29 085

REPORT DOCUMENTATION PAGE

OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 2050

1. AGENCY USE ONLY *(Leave blank,*

2. REPORT DATE
June 30, 1994

3. REPORT TYPE AND DATES COVERED
Technical Report # 22

4. TITLE AND SUBTITLE
Radical Polymerization of Vinyl Acetate In The Presence of Trialkyl Phosphites

5. FUNDING NUMBERS
N00014-94-1-0101

6. AUTHOR(S)
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Carnegie Mellon University
Department of Chemistry
4400 Fifth Avenue
Pittsburgh, PA 15213

8. PERFORMING ORGANIZATION REPORT NUMBER
N00014-94-1-0101

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Department of the Navy
Office of Naval Research
800 North Quincy Street
Arlington, VA 22217-5000

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
Technical Report #22

11. SUPPLEMENTARY NOTES
ACS Polym. Preprints, 35(1), 466 (1994)

12a. DISTRIBUTION/AVAILABILITY STATEMENT

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

Radical polymerization of vinyl acetate initiated by BPO in the presence of different phosphites was studied. As it was observed, trialkylphosphites enhance polymerization rates. The molecular weights of polymers are affected by the initiator concentration and can be adjusted to higher or lower values. Polydispersities do not change with conversion and are lower than for PVAc obtained with BPO as an initiator (usually $M_w/M_n = 1.6$ to 1.7 for BPO/TFEP as an initiating system.). The presence of pentavalent phosphorous atoms in the BPO/TFEP system as well as in polymer obtained with that system was revealed by ^{31}P-NMR spectroscopy.

14. SUBJECT TERMS

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	**18. SECURITY CLASSIFICATION OF THIS PAGE**	**19. SECURITY CLASSIFICATION OF ABSTRACT**	**20. LIMITATION OF ABSTRACT**
Classified	Classified	Classified	UL

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18
298-102

RADICAL POLYMERIZATION OF VINYL ACETATE IN THE PRESENCE OF TRIALKYL PHOSPHITES

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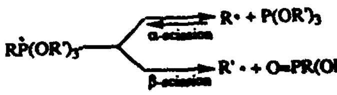
Introduction

Reactions involving free radicals and trivalent phosphorus compounds such as alkyl (aryl) phosphines or phosphites have been intensively studied in recent years[1]. The reaction products were often identified as phosphoranyl radicals, which may undergo subsequent α or β-scissions (eq. 1,2)[2]:

$$R\cdot + P(OR')_3 \longrightarrow R\dot{P}(OR')_3 \qquad (1)$$



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The former reaction is usually an opposite reaction to the formation of phosphoranyl radical, whereas the latter one is the oxidation process which leads to the formation of P=O bonds, like in Arbuzov rearrangement. There are a few examples of radical polymerization of some acrylic monomers (methyl methacrylate, acrylonitrile) in the presence of trivalent phosphorus compounds (phosphines, phosphites)[3,4]. A monomer:PR_3 complexation affects the polymerization kinetics, whereas molecular weights and polydispersities are not influenced by the initiator/phosphorus ratios.

In this paper we report on the radical polymerization of vinyl acetate (VAc) initiated by benzoyl peroxide (BPO) in the presence of phosphites or phosphates. Molecular weights and polydispersities of poly(vinyl acetate) prepared by initiation with (BPO)/tris(2,2,2-trifluoroethyl)phosphite system do not vary with conversion. In contrast, when BPO alone was used as initiator, a strong decrease in molecular weights with conversion was noticed, as well as a significant increase in polydispersities (Mw/Mn = 1.4 to 1.95). Higher concentrations of initiator lead to lower molecular weights, independently of the initiator/phosphite molar ratios.

Results and Discussion

Polymerization rates increase in the presence of tris(2,2,2-trifluoroethyl)phosphite (TFEP). Figure 1 presents time-conversion plots in semilogarithmic coordinates for polymerization of VAc, initiated by TFEP/BPO (1.5/1) and BPO alone. at the same concentration of peroxide (0.025M). The kinetic plots obtained in the presence of phosphite are linear, indicating that the concentration of the growing radicals does not vary during polymerization.

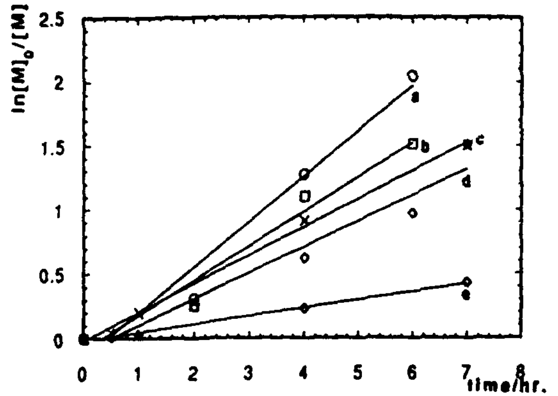

Figure 1. Time-conversion plots in semilogarithmic coordinates in polymerization of VAc initiated by BPO/TFEP(1/1.5) and BPO alone, $[VAc]_0$ = 5.4M, benzene, 60°C, $[BPO]_0:[TFEP]_0$= 1:1.5, (a) $[BPO]_0$ = 0.11M, (b) $[BPO]_0$ = 0.08M,(c) $[BPO]_0$ = 0.05M, (d) $[BPO]_0$ = 0.025M, (e) $[BPO]_0$ = 0.025M, no TFEP

Figure 2 presents effect of added TFEP on the variation of molecular weights with conversion for polymerization of VAc initiated by BPO at 60°C. In polymerization initiated by BPO alone, molecular weights decrease with conversion. This can be ascribed to the much stronger decrease of the propagation rate in comparison with the initiation rate. Polymerization degrees, defined by the ratio of the corresponding rates (assuming no contribution of transfer) decreases gradually with conversion. In contrast, polymerization in the presence of phosphites provides constant value of the molecular weight during entire polymerization process. Molecular weights are, however, affected by the concentration of phosphite/BPO initiating system. Higher molecular weights are observed at lower initiator concentration.

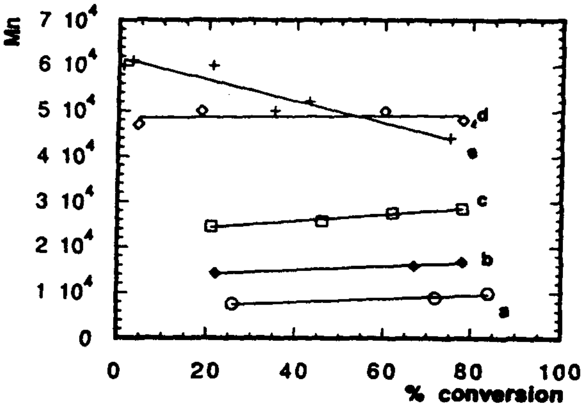

Figure 2. M_n-conversion dependence in polymerization of VAc initiated by TFEP/BPO ($[VAc]_0$ = 5.4M, benzene, 60°C, $[BPO]_0:[TFEP]_0$= 1:1.5, (a) $[BPO]_0$ = 0.11M, (b) $[BPO]_0$ = 0.08M,(c) $[BPO]_0$ = 0.05M, (d) $[BPO]_0$ = 0.025M, (e) $[BPO]_0$ = 0.025M, no TFEP

Variation of molecular weights with conversion for the initiation with BPO alone leads to the increase of polydispersities. Initially, low values in the range of M_w/M_n=1.5 may indicate termination by coupling, as expected for polymerization of vinyl acetate[5]. Polydispersity increases strongly with conversion (to $M_w/M_n > 2$), because molecular weights decrease due to the reduction of the ratio rate of propagation/rate of initiation. Surprisingly, polydispersities in the presence of phosphite do not change during entire polymerization (M_w/M_n = 1.6 to 1.7), as shown in Figure 3

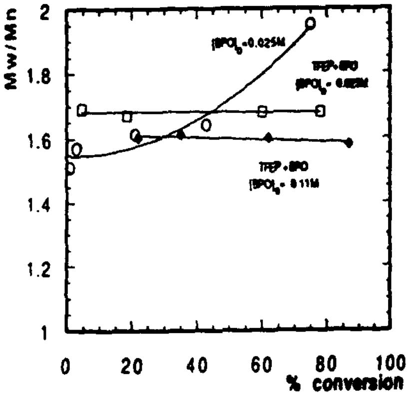

Figure 3 M_w/M_n - conversion dependence in polymerization of VAc initiated by TFEP/BPO (1.5/1)

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Structure of phosphites strongly affect polymerization of vinyl acetate initiated by BPO. Table 1 shows the influence of different phosphites on polymerization of VAc in benzene at 60°C.

Table 1
Effect of the Structure of Phosphites on Polymerization of Vinyl Acetate in Benzene at 60°C [a)]

Phosphite	M_n	M_w/M_n	Conversion, %
$(CH_3O)_3P$	99,000	1.55	18
$(n\text{-}C_4H_9O)_3P$	84,000	1.56	5
$(i\text{-}C_3H_7O)_3P$	-	-	< 0.5
$(CF_3CH_2O)_3P$ [b)]	63,000	1.39	85

a) $[P(OR)_3]_o/[BPO]_o = 1.5/1$, $[BPO]_o = 0.025$ mol/L, $[VAc]_o = 7$ mol/L, 24 hours
b) time = 6 hours

Polymerization rates are probably affected by both steric and electronic factors. Rates are strongly reduced by the increase of the size of alkyl group in the phosphite (Me<Bu<iPr). However, trifluoroethyl group has the intermediate size but provides the fastest polymerization. This could be ascribed to the electronic effects.

Replacement of a trivalent trimethyl phosphite, $(CH_3O)_3P$, with a pentavalent trimethyl phosphate $(CH_3O)_3P{=}O$, leads to a strong increase of the rate and polydispersity and change of the molecular weight (after 24 hours - 83% conversion; $M_n = 27{,}000$; $M_w/M_n = 2.72$). These data are very similar to the polymerization initiated by BPO alone. This may indicate that phosphates have very small effect on polymerization of vinyl acetate, in contrast to phosphites.

In order to get a deeper insight into the nature of the initiating system, the reaction of TFEP with BPO (1.5/1) was followed by ^{31}P-NMR. At room temperature after 0.5 hours no reaction was observed and only the original signal of TFEP at 139 ppm was detected. When the reaction temperature was increased to 60°C, after 0.5 hours a new signal of pentavalent phosphorous ($\delta = -2.6$ ppm) was found. Figure 4 shows the ^{31}P-NMR spectrum of this reaction mixture.

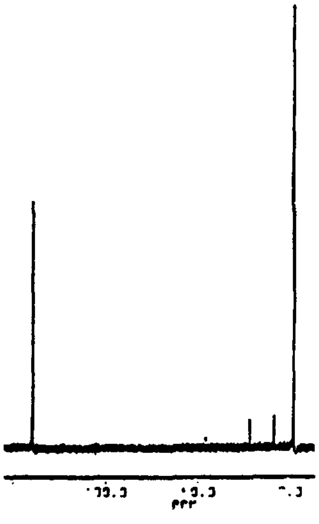


Figure 4. ^{31}P-NMR spectrum of the products of the reaction of TFEP with BPO (1.5/1) at 60°C after 0.5 hours, $CDCl_3$

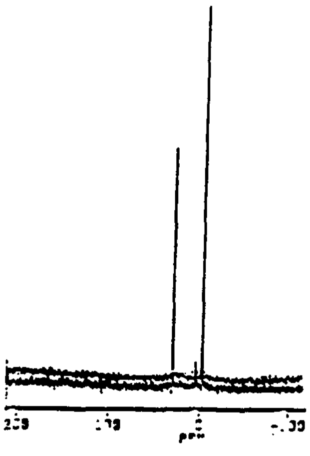
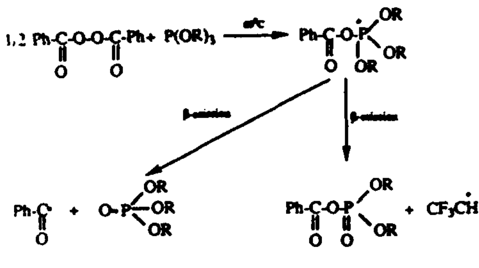


Figure 5. ^{31}P-NMR spectrum of PVAc (Mn=8,000), $CDCl_3$

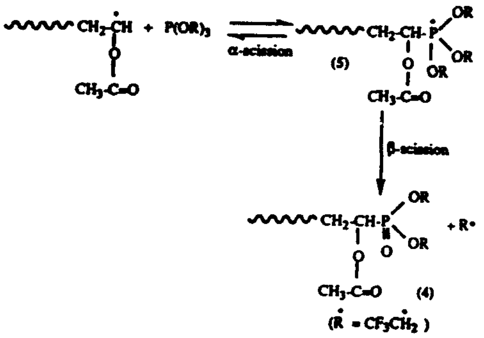
The initiation process can be described as follows:



(3)

So, either trifluoroethyl radicals $CF_3CH_2\cdot$ or benzoyl radicals $PhCO\cdot$ may initiate polymerization of VAc. It is also possible that the initiation may involve direct reaction between phosphoranyl radicals and monomer. If such a bimolecular reaction will be the slowest one (rate determining) in the entire initiation process, then the propagation and initiation rates will be affected in the same way by the changes in monomer concentration. In that case the molecular weight will not change with conversion resulting in lower polydispersities.

^{31}P-NMR spectra recorded on PVAc polymers ($M_n = 8{,}000$) (Fig.5) revealed the presence of pentavalent phosphorus atoms at $\delta = 30$ ppm. This is the range of absorption of dialkyl alkylphosphonates [$(RO)_2P(O)R'$]^6. It is possible that these functions can be incorporated by transfer processes:



The bond energy of the P-O bond is higher than that of the P-C bond (e.g. 86 kcal/mole vs. 65 kcal/mole)^6. Initially lower molecular weights observed in system with phosphites in comparison with initiation with BPO alone may additionally support this type of a reaction.

Acknowledgments

Acknowledgment is made to the Office of Naval Research and to the National Science Foundation, via the support within Presidential Young Investigator Award to K.M., as well as to Du Pont, Eastman Kodak, PPG Industries and Xerox Corporation for the matching funds.

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