Polymer Bulletin 15, 127–134 (1986)

Polymer Bulletin

Purification Methodology

Preparation of High Purity, Anionic Polymerization Grade Alkyl Methacrylate Monomers

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SUMMARY

A method has been developed which provides very pure alkyl methacrylate monomers for anionic polymerization. This method takes advantage of the chemistry of trialkylaluminum compounds-their reactivity with alcohols and moisture, and their complex formation with methacrylic esters which facilitates titration of impurities. When coupled with previously known polymerization techniques, this purification methodology allows for both the synthesis of narrow distribution poly(alkyl methacrylates) of controlled and predictable molecular weight and for the utilization of a wide variety of methacrylate monomers. The procedure described herein should be equally applicable to group transfer polymerization.

INTRODUCTION

The advent of anionic "living" polymerization in the late 1950's led to developments in synthetic control approached by few other polymerization mechanisms. Parameters such as molecular weight, molecular weight distribution, stereochemistry, chain end functional groups, polymer architecture and sequence distribution may ideally be controlled with anionic polymerization [1-5]. Anionic polymerization of alkyl methacrylates, especially methyl methacrylate, has been studied extensively over the last two decades [6-10]. The vast majority of these investigations have dealt with the kinetic and mechanistic aspects of anionic methacrylate polymerization. However, relatively few investigations have been concerned with the synthesis of novel homo- and copolymers [11-13]. Two major reasons why synthetic studies of these systems have lagged behind the voluminous work done on the hydrocarbon monomers, e.g. styrene, butadiene and isoprene, are problems with methacrylate monomer purity and the inherent side reactions found in most anionic polymerizations involving polar monomers. The problem of side

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reactions to the methacrylate carbonyl has been well documented in the literature [14]. Methods have been developed in the past to avoid these deleterious side reactions, namely bulky initiators, low temperatures and polar solvents. This has enabled various investigators to synthesize narrow distribution poly(alkyl methacrylates) by utilizing the well established polymerization route of the polar solvent (THF) at -78°C with the bulky initiator diphenyl hexyl lithium (DPHL). The problem of monomer purification has been a much less appreciated aspect of the anionic synthesis of methacrylate polymers. Suitable methods are available for the scrupulous purification of hydrocarbon monomers. For example, the organometallic reagent dibutyl magnesium (DBM) has been well documented as a highly sensitive reagent which reacts with the last traces of water, air, or most other terminating impurities present in styrenic and diene monomers [15]. The presence of a bright yellow complex is a useful indicator, assuring the chemist that the monomer is highly pure. Unfortunately, DBM and most other similar compounds rapidly polymerize alkyl methacrylates.

Calcium hydride is currently the established purification agent for methacrylate monomers. This "drying agent" falls short in two respects concerning methacrylate purification. First, due to the heterogeneous nature of calcium hydride dispersed in a polar monomer such as methyl methacrylate, the somewhat hydrophilic MMA may be difficult to fully dry. More importantly, higher methacrylate monomers are generally synthesized via transesterification of MMA with the appropriate alcohol. In most cases the alcohol has a boiling point relatively close to the resulting methacrylate, which ensures that alcoholic, terminating impurities are present in virtually all commercially available methacrylates. Calcium hydride unfortunately does not react with these alcohols and, indeed, is listed as a drying agent for alcohols in some organic texts. Thus, most alkyl methacrylates cannot be used for anionic polymerization with any degree of success. This is especially true when high molecular weight polymers (ca. 10^5) are desired. This places severe limitations on the potential properties one may obtain via anionic methacrylate polymerization.

A new purification method involving trialkyl aluminum reagents has thus been developed in our laboratories for the purification of alkyl methacrylates. This technique allows for both the synthesis of narrow distribution poly(alkyl methacrylates) of controlled and predictable molecular weights and for the utilization of a wide variety of methacrylate monomers. In addition, judicious choice of the polymerization solvent permits control of polymer stereochemistry. We have taken advantage of both variables (ester alkyl group and polymerization solvent) and utilized these rigorously purified monomers to synthesize poly(alkyl methacrylate) homo- and copolymers with a wide range of physical properties, from glasses to semi-crystalline systems, and even elastomers [16-18]. In this communication, we will present a detailed description of this purification procedure. Data will be presented which shows the utility and applicability of this procedure for the preparation of alcohol-free, anionic polymerization grade methacrylate monomers.

EXPERIMENTAL

Materials:

The alkyl methacrylate monomers were products of either Rohm and Haas Co. or Polysciences, Inc. Methyl methacrylate (MMA) was obtained from Rohm and Haas Co.

The polymerization solvent tetrahydrofuran (THF) (Fisher, Certified Grade) was purified by double distillation from the purple sodium/benzophenone ketyl.

The initiator components 1,1-diphenyl ethylene (DPE) and sec-butyl lithium are products of Eastman Kodak Co. and the Lithco Division of FMC, respectively. DPE was purified by distillation from n-butyl lithium. Sec-butyl lithium was used as received, however the molarity can be determined using the Gilman "double titration" method [19].

The alkyl aluminum purification agents triethyl (TEA) and tri-n-octyl (TOA) aluminum were generously provided by the Ethyl Corporation; they are packaged as 25 wt.% solutions in hexanes and were used as received.

Methacrylate Purification:

The monomer as received was stirred and degassed over finely ground calcium hydride (CaH_2) under nitrogen for several days, then distilled under vacuum to remove traces of water, inhibitor, polymer, and oxygen. This "conventionally pure" monomer was then transferred into a dry, nitrogen purged, septum capped brown glass bottle for relatively long term storage in a -20°C freezer. When needed, desired quantities of this CaH_2-pure MMA can be transferred into the nitrogen filled monomer purification apparatus shown in Figure 1 via syringe or cannula.

The glassware involved in this apparatus is generally baked out in a glass annealing oven at a maximum temperature of 575°C prior to use. After rinsing with distilled water, it was placed in a drying oven overnight (110°C). The glassware was assembled while still hot, followed by vigorous flaming under vacuum (10^{-2} torr). A vacuum-flame-nitrogen purge cycle was performed three times prior to filling the apparatus with nitrogen. The nitrogen had been previously purified by passing through columns containing 4Å sieves, 13x sieves, and CaH_2. The CaH_2-pure MMA was added to flask A through a rubber septum and three-way valve C using a syringe or cannula. The monomer was then degassed several times using standard freeze-thaw techniques. It is important that utmost care should be taken to remove all the oxygen before the addition of trialkyl aluminum, since it is known that in the presence of oxygen, trialkyl aluminums will lead to free radical polymerization of MMA [20]. In our experience, if the MMA is not carefully degassed, less than 50 percent of the monomer will be recovered by distillation. However, when careful precautions are taken, virtually all of the MMA is recovered after distillation.

To the "conventionally pure" and scrupulously de-oxygenated MMA is then slowly added very small increments of the trialkyl aluminum in hexane solution. The aluminum alkyl is added slowly to the stirring MMA so as to avoid both exotherms and more importantly, local concentration buildup of alkyl aluminum in MMA, as these conditions may lead to reactions of the ester group [21-22]. The use of diluted alkyl aluminum is suggested in these regards which also simplifies handling the highly pyrophoric bulk TEA. Diluted TEA is only mildly pyrophoric, and diluted TOA is quite air insensitive. After the alcohol and other protic impurities have reacted with the alkyl aluminum, complex formation will rapidly take place with addition of more alkyl aluminum, producing a bright yellow endpoint. This straightforward behavior is witnessed with the simple ester containing methacrylates derived from primary alcohols, e.g. methyl, ethyl, n-butyl. More unusual behavior is apparent when branched (secondary and tertiary) methacrylates are employed, e.g. isopropyl, cyclohexyl, and t-butyl methacrylates [16,23]. After the endpoint is reached, 10-30 percent more

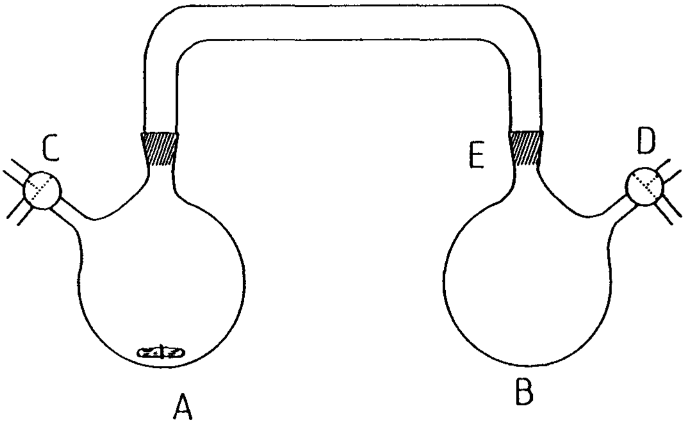


Figure 1. Vacuum Distillation Apparatus for Methacrylate Monomer

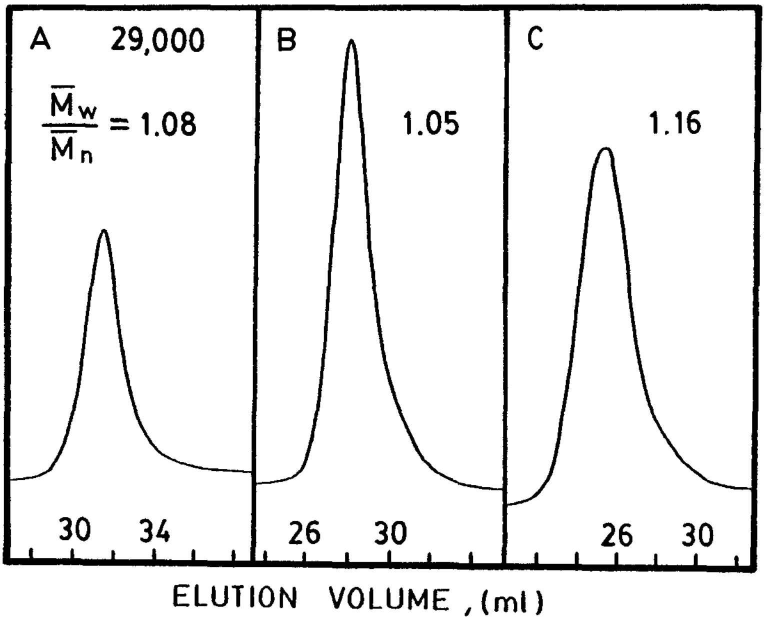


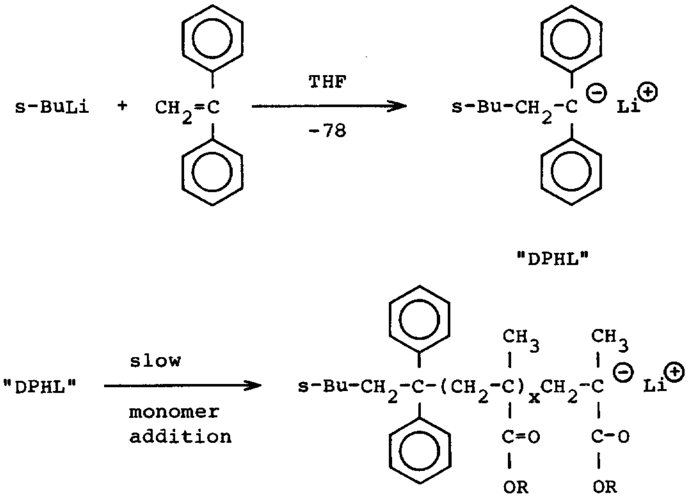
Figure 2. GPC Chromatograms of:
A) PMMA Calibration Standard
B) PMMA from "Undoped" MMA, TEA Treated
C) PMMA from NPA-"Doped" MMA, TEA Treated

TEA (or TOA) is then added which produces a more intense yellow color. It should be mentioned that we are still working with a very low molar concentration of trialkyl aluminum, typically 1-5 mole percent based on the monomer, depending on the inherent impurity, i.e. alcohol content, of the "CaH_2-pure methacrylate" monomer.

Polymer Synthesis:

All polymerizations were conducted under the inert atmosphere conditions necessary for non-terminating anionic polymerizations. Prepurified nitrogen gas was most commonly used in this work. It was further purified and dried by passing through two 3 ft. columns of 4Å molecular sieves, 13x sieves, and calcium hydride as described earlier.

Alkyl lithium initiators based on 1,1-diphenyl ethylene have been demonstrated [24-25] to be efficient initiators for anionic methacrylate polymerization due to the hindered, less basic nature of the anion especially in comparison to more reactive alkyl lithiums (e.g. butyl lithium). Thus, as shown in Scheme 1, diphenyl ethylene (2-4 mmoles) was added to 25 - 50 mls of purified THF in a round bottom polymerization flask. After cooling the flask to -78°C the desired amount of s-butyl lithium (1 mmole) was then charged. The purified monomer was then slowly added to the initiator solution. Fast initiation is evident even at -78°C, as the red color disappears after the first few drops of monomer have been added. Experience indicates that if the monomer and THF are of extreme purity, the polymerizing methacrylate anion is colorless. The remaining monomer was added in a very slow, dropwise fashion to avoid exotherms which would cause side reactions. Calculations of monomer and initiator charged are based on both the desired molecular weight and the preferred percent solid level. After completion of the monomer addition, the polymerization is terminated after several minutes by adding a small amount of an acetic acid/methanol mixture. The polymers are then precipitated in an appropriate non-solvent.

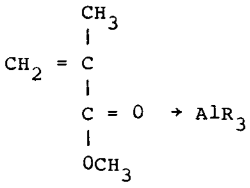


Scheme I. Anionic Synthesis of Poly(alkyl methacrylates).

All polymers were analyzed for molecular weight and molecular weight distribution primarily by size exclusion chromatography (SEC). A variable temperature Waters 150-C GPC equipped with microstyragel columns with porosities of 500Å, 10^3Å, 10^4Å, 10^5Å and 10^6Å was employed. PMMA standards (Polymer Laboratories) were utilized for the construction of calibration curves in all cases. A sensitive UV-Visible method for Mn has also been developed for these systems based on the presence of one DPH (1,1-diphenyl-3-methyl pentyl) residue per chain [23].

RESULTS AND DISCUSSION

After experiencing difficulty in gaining consistent polymerization results, especially with the higher alkyl methacrylates, it was decided that the search for a new purification technique should be initiated. As residual alcohols are the major impurity in most alkyl methacrylates, purification agents which react with alcohols (and water) but do not react with methacrylates were sought. Initial experiments were conducted with conventional organic alcohol scavengers such as calcium chloride ($CaCl_2$) and 5Å molecular sieves. More intriguing, however, was the possibility of using trialkyl aluminums as methacrylate purification agents. This idea stemmed from a series of papers by P.E.M. Allen, et al. [20-22] in which triethyl aluminum (TEA) was investigated as a possible initiator for methacrylate polymerization. Although radical polymerization of MMA may occur by photoinitiation, anionic polymerization does not occur. It was also found that if an excess of MMA is present, a stable yellow complex of the structure 1 was formed. Allen and Moody also tried triethyl aluminum as a final purification of MMA before a dilatometry experiment [26], but then turned to the heterogenous sodium benzil purification which appeared to be more amenable to high vacuum work [27].



$$CH_2=C(CH_3)-C(=O\rightarrow AlR_3)-OCH_3$$

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These factors lead to the belief that trialkyl aluminums reagents might serve as purification agents for methacrylate monomers, as the requirements for the ideal methacrylate purification agent are:

1. No reaction with or polymerization of methacrylates.
2. Rapid reaction with alcohols and water.
3. Rapidly forms color upon total purification of most methacrylate monomers, i.e. the methacrylate impurities can be titrated.

The reactive properties of trialkyl aluminums with alcohols and water are well known [28]. A combination of the above facts lead to the utilization of trialkyl aluminums for methacrylate purification.

As a model system which represents an impure methacrylate, MMA "doped" with n-propyl alcohol (NPA) was chosen. This combination was arrived at due to the relative hydrophilicity and availability of MMA, and more importantly, the very close boiling points of NPA and MMA (97° and 100°C, respectively). Thus, no possibility existed for separation by simple distillation. A stock solution was prepared which contained 96% MMA and 4% NPA. The heterogeneous purification agents were allowed to interact with an aliquot of this stock solution for one week. After filtration (when necessary) the solution was distilled under vacuum and the resulting product was slowly added to a solution of DPHL initiator in THF at -78°C.

TABLE 1

Purification Study on n-Propyl Alcohol Doped Methyl Methacrylate

EXPT	AGENT	Remarks
1	CaH_2	No Polymer
2	$CaCl_2$	No Polymer
3	5Å Sieves	No Polymer
4	Triethyl Aluminum	100% yield

As seen in Table 1, no polymer was formed in the CaH_2 "control" experiment or in the purification attempts with the conventional scavengers (experiments 1-3). Analysis of the distillate by GLC showed NPA levels virtually unaffected by these "scavengers". Consequently, no polymer was produced when these alcohol-laden monomers were slowly added to the initiator solution. The results of experiment 4 using triethyl aluminum titration proved quite different, however. After slow addition of a substantial amount of the alkyl aluminum solution, a bright yellow endpoint was observed. GLC analysis of the distillate confirmed the absence of NPA and the presence of only MMA and hexane diluent. The polymer formed in quantitative yield from experiment 4 showed a fairly narrow polydispersity from GPC analysis. This chromatogram is shown in Figure 2. Also shown is a PMMA resulting from TEA purification of "undoped" MMA. These polymers are in the molecular weight range of 50-70,000 g/mole, were both synthesized quantitatively, and exhibited the narrow polydispersities associated with non-terminating polymerization. Also included is a PMMA standard (Polymer Labs) of slightly lower molecular weight.

Having the capability to scrupulously purify alkyl methacrylate monomers, the major research objectives include the synthesis of poly(alkyl methacrylates) with predictable and controllable molecular weights with fairly narrow molecular weight distributions, and high molecular weights (if desired), and the synthesis of methacrylate containing block copolymers of high structural integrity. These goals have been accomplished, and will be the subject of future publications [16,17,23,29].

ACKNOWLEDGMENT

The authors would like to thank Dr. Thomas G. Hanlon of Ethyl Corporation for the generous donation of alkyl aluminum reagents and his advice on their chemistry and Dr. Robert A. Patsiga of Indiana University of Pennsylvania for his helpful technical discussions. The authors also would like to thank the Dow Chemical Co. and the Exxon Foundation for supporting this research.

References

1. M. Szwarc, M. Levy, and R. Milkovich, J. Am. Chem. Soc. 78, 2656 (1956).
2. M. Szwarc, "Carbanions, Living Polymers and Electron Transfer Processes," Interscience, New York, (1968).
3. J. E. McGrath, ed., "Anionic Polymerization: Kinetics, Mechanisms and Synthesis," ACS Symposium Series, No. 166, (1981).
4. M. Morton, "Anionic Polymerization: Principles and Practice," Academic Press, New York, 1983.
5. R. N. Young, R. P. Quirk, and L. J. Fetters, Advances in Polymer Sci. 56, 1 (1984).
6. T. G. Fox, B. G. Garrett, W. E. Goode, S. Gratch, J. F. Kincaid, A. Spell, J. D. Stroupe, J. Am. Chem. Soc. 80, 1768 (1958).
7. D. M. Wiles, "Structure and Mechanisms in Vinyl Polymerization," Eds. T. Tsuruta K. and F. O'Driscoll, Marcel Dekker, New York, Chapter 8 (1969).
8. H. Yuki and K. Hatada, Advances in Polymer Sci. 31, 1 (1979).
9. A. H. E. Muller, "Anionic Polymerization: Kinetics, Mechanisms, and Synthesis," ed. J. E. McGrath, ACS Symposium Series, No. 166, 441 (1981).
10. P. E. M. Allen and D. R. G. Williams, Ind. Eng. Chem. Prod. Res. Dev. 24, 334 (1985).
11. B. C. Anderson, G. D. Andrews, P. Arthur, H. W. Jacobson, L. R. Melly, A. J. Playtis, and W. H. Sharkey, Macromolecules 14, 1599 (1981).
12. P. Lutz, P. Masson, G. Beinert, and P. Rempp. Polymer Bulletin 12, (1984).
13. T. Q. Nguyen and H. H. Kausch, Makromol. Chem., Rapid Commun. 6, 391 (1985).
14. K. Hatada, T. Kitayana, K. Fumikana, K. Onta, and H. Yuki, "Anionic Polymerization: Kinetics, Mechanisms, and Synthesis," ed. J. E. McGrath, ACS Symposium Series, No. 166, 327 (1981).
15. M. Morton and L. J. Fetters, Rubber Reviews 48, 359 (1975).
16. R. D. Allen, Ph.D. Thesis, Virginia Polytechic Institute and State, Blacksburg, VA 24061 (1985).
17. R. D. Allen and J. E. McGrath, Polymer Preprints 25(2), 9 1984; R. D. Allen, T. E. Long and J. E. McGrath, in "Adv. in Polymer Sym. B. M. Culbertson and J. E. McGrath Edit, Plenum, 1985.
18. R. D. Allen, S. D. Smith, T. E. Long, and J. E. McGrath, Polymer Preprints 26(1), 247 (1985).
19. H. Gilman and F. K. Cartledge, J. Organometal. Chem. 2, 447 (1964).
20. P. E. M. Allen and B. A. Casey, Eur. Polym. J. 2, 9 (1966).
21. P. E. M. Allen and B. A. Casey, Eur. Polym. J. 6, 793 (1970).
22. P. E. M. Allen, B. A. Bateup, and B. A. Casey, J. Organometall. Chem. 29, 185 (1971).
23. T. E. Long and J. E. McGrath, to be published.
24. D. Freyss, P. Rempp and H. Benoit, J. Polym. Sci. Letters, 2, 217 (1964).
25. D. M. Wiles and S. Bywater, Trans. Fara. Soc. 61, 150 (1965).
26. P. E. M. Allen and B. Moody, Makromol. Chem. 81, 237 (1965).
27. P. E. M. Allen, private communication.
28. T. Mole and E. A. Jeffrey, "Organo-Aluminum Compounds," Elsevier, Amsterdam, (1972).
29. J. E. McGrath, et al Polymer Preprints 27(1), 000 1986.

Accepted January 15, 1986

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