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"Speed" Marvel at DuPont

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INTRODUCTION

Before beginning the technical subject, I'd like to take a few minutes to review Professor Marvel's long association with DuPont. Professor Marvel is known simply as "Speed" at DuPont, and I will refer to him by that title of respect. Speed has been a consultant for DuPont since February 1928, a little more than 55 years. In that time, we estimate he has made 260 trips to Wilmington or other DuPont locations from Urbana and Tucson, held 19,000 individual consulting conferences, stayed 1308 nights in the DuPont hotel (= 3.58 years), and surely, established many records for a consulting relationship, both in duration and breadth.

We at DuPont owe him much for his prodigious efforts on our behalf. Speed has brought other things than chemistry to us. He has popularized birding, catching the spring and fall migrations; in fact, he did that Monday. He also brought some new poker games to Wilmington, including one called "Benzene." We don't owe him for that, we've already paid.

Speed has made many contributions to DuPont: Technical, administrative, and training students.

> Forty of his 176 graduate students joined DuPont as did many of his about 150 postdoctoral students. Many undergraduates at Illinois were influenced to study chemistry by Speed and later joined DuPont, and I am one of those.

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Speed has always been committed to improving research effectiveness and organization in DuPont, and throughout his consulting career contributed significantly to the present system of research administration. Speed is widely known as a friend and advocate of the chemist's point of view.

Technically, Speed is legendary for his ability to recall pertinent detailed references, both inside and outside DuPont. It seems likely that in the period when he was working 30 days/year at DuPont and visiting many different labs, he had a better overall grasp of DuPont polymer chemistry than anyone else. Perhaps his best known specific suggestion was that amide solvents would work for polyacrylonitrile–a line of research that led to Orlon.

Speed, of course, interacted with many of DuPont's pioneers in polymer science: C. M. A. Stine, who envisioned polymer chemistry as an important field for DuPont research; Wallace Carothers, who implemented the program and guided it to its first fruition; Arnold Collins, who found neoprene in a receiver of his still; Julian Hill, who "discovered" cold drawing and thus made the first man-made fiber, a polyester; Jerry Berchet, who made the first 66 nylon; Bob MacDonald, who end-capped polyformaldehyde; and many, many more.

Speed has always been an involved and participative consultant, and a documented anecdote from 1928 will serve to illustrate this deep involvement with organic and polymer chemistry in DuPont.

On February 1, 1928, Speed signed an employee agreement and became a consultant for the old Chemical Department at the Experimental Station. On February 6, 1928, Wallace Carothers, whom Speed knew from the University of Illinois, joined that organization to begin his seminal research on polymers. On February 16, 1928, Speed wrote to Carothers that he thought Carothers' plan to study polyesterification and polyamidation was a good one and discussed the availability of intermediates. On March 8, 1928, Speed sent another letter offering 1 kg of adipic acid to Carothers for $30.00, thereby probably supplying him with his first adipic acid. So, Speed was present at the beginning of polymer chemistry at DuPont, and through to the present day.

I feel honored to forward the congratulations of his many colleagues at DuPont to Speed on the occasion of his honorary degree from the famous Polytechnic Institute of New York. Well done, Speed.

ANIONIC POLYMERIZATION OF METHACRYLATES

The research I will describe today was done in the Central Research Department of DuPont to demonstrate polymer chemistry, which we hoped could be the basis of new organic coatings, capable of meeting new functional, aesthetic, processing, and regulatory requirements. Many of today's new polymer systems represent a third generation of products in which the polymeric product meets both stringent property requirements of the user and the needs of sophisticated processing equipment in an economically efficient way. We hoped that anionic polymerization of acrylates and methacrylates could be demonstrated which would allow improved control of molecular parameters; for example, comonomer distribution, molecular weight, molecular weight distribution, endgroup functionality, and branching when compared to the conventionally used radical polymerization.

The reactions which must be controlled are shown in Fig. 1. Initiation of, for example, methyl methacrylate by an anionic initiator is a Michael reaction and propagation consists of consecutive additional Michael reactions with the polymethyl methacrylate anion.

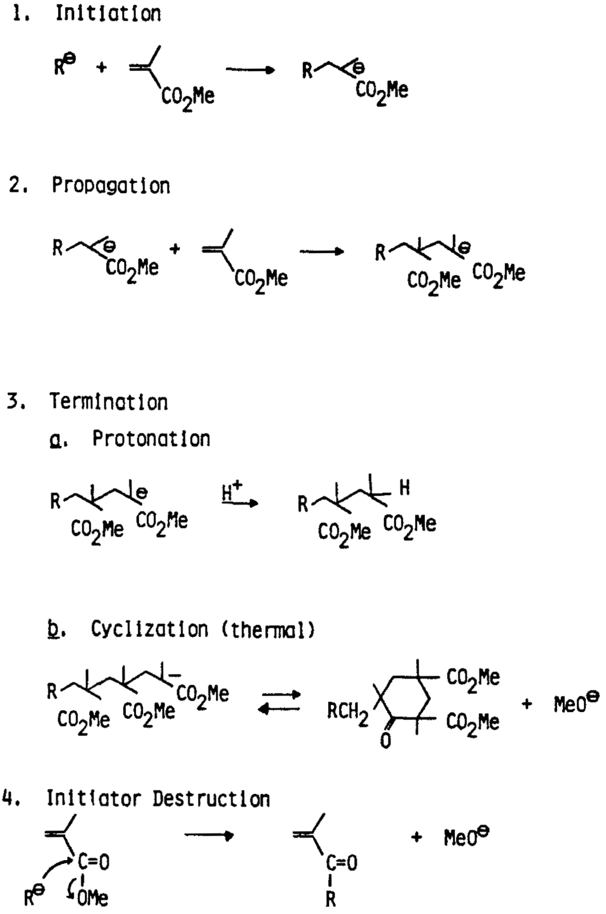
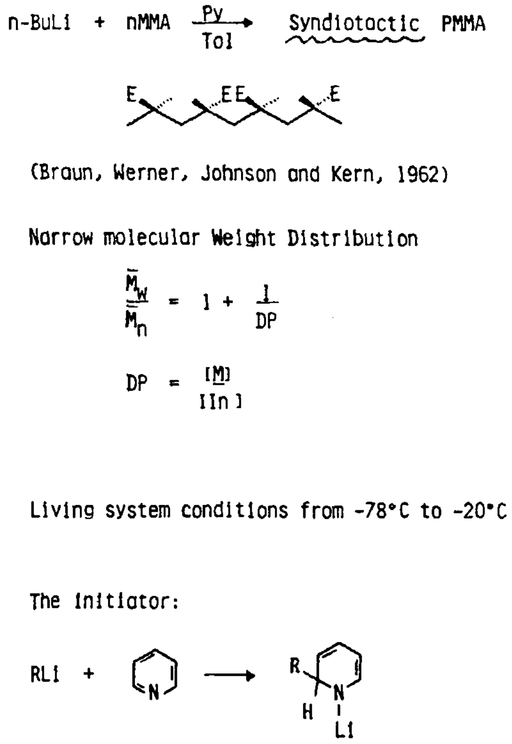


FIG. 1. Anionic polymerization.

Protonation by impurities, solvent, monomer, or polymer must be completely avoided, of course. In addition, a chain transferlike process can occur if the PMMA anion undergoes a Claisen-type condensation forming the cyclic ketone shown and freeing methoxide ion. Methoxide ion is a relatively poor initiator, but the damage is already done if the cyclization occurs, and this reaction is a limiting factor. Another reaction which must be avoided is initiator destruction, and many initiators are unsatisfactory because they react partially in this manner. To our knowledge, no system previously reported indicated all of these conditions could be met.

The first lead which showed promise of meeting our needs came when we reinvestigated the pyridine/butyllithium system reported by Braun and co-workers for the preparation of highly syndiotactic PMMA (Fig. 2). At -78°C in toluene, very narrow molecular weight distributions were obtained with degree of polymerization approximately equal to moles of monomer divided by moles of initiator. NMR



$$\text{n-BuLi} + \text{nMMA} \xrightarrow[\text{Tol}]{\text{Py}} \text{Syndiotactic PMMA}$$

(Braun, Werner, Johnson and Kern, 1962)

Narrow molecular Weight Distribution

$$\frac{\bar{M}_w}{\bar{M}_n} = 1 + \frac{1}{DP}$$

$$DP = \frac{[M]}{[In]}$$

Living system conditions from -78°C to -20°C

The initiator:

FIG. 2. Methacrylate initiation with alkyllithium reagents in toluene/pyridine at -78°C.

investigation of low molecular weight products showed the initiator to be formed by addition of n-BuLi to pyridine as shown at the bottom of Fig. 2.

Optimization of this system led to use of sec-butyllithium and pyridine in THF (Table 1). With careful temperature control as shown in Lines 1 and 3, very narrow MWD's were obtained, yielding numbers below the theoretical 1.0 when GPC columns calibrated with polystyrene were used to estimate MWD. Broadening occurred at -20° C, but we became convinced that under the best conditions, initiator destruction, cyclization, and protonation could all be avoided. The pyridine system was undesirable, however, because pyridine was difficult to remove from low MW products and the dihydropyridyl ends were unstable, tending to discolor, especially on heating.

The next advance occurred when the diphenylhexyllithium initiator of Wiles and Bywater was tried in THF with careful temperature control. Comparison of Theoretical DP's in the left column of Table 2 with actual DP's shows that this system has the control we require. NMR was exceptionally useful for calculating DP's at lower molecular weights, the ten aromatic protons of the DPPH initiator being compared with methacrylate C or O methyl resonances of the polymer. Once again, lower than possible MWD's were obtained using columns calibrated with polystyrene. This system allowed us to demonstrate the living nature of the PMMA anion with delayed addition, preparation of block polymers and NMR studies of some systems; for example, the anion obtained from t-butyl methacrylate, which is living to -20° C.

Table 3 shows an example of preparation of block polymers; a live PMMA anion of 200 DP was prepared and used to prepare two A.B. block polymers with lauryl methacrylate and an A.B.A. example. You can see that MWD's are broadened, but purified samples show the T_g's expected for A.B. and A.B.A. block polymers.

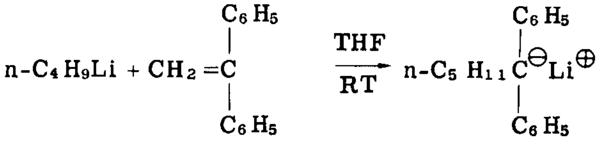
We next studied capping reactions of the anion. Table 4 lists successful capping agents which are limited, in general, to reactive halides; all but one are bromides and iodides. The reason reactive halides are needed is that the reactions must proceed at -78° C; any significant temperature rise leads to the cyclization reaction and much reduced yields. The best reactions were obtained with bromomethyl aromatic compounds, so we investigated bis-bromomethyl compounds as coupling agents. Analysis by comparison of molecular weight data in Table 5 looked promising, but the broadening of MWD was not encouraging and further proof was certainly required. The last line shows that the reactions do involve the anion, since protonation prevents coupling completely. With the DPPH initiator system, Table 6, somewhat better results were obtained and polyfunctional compounds also showed increases in molecular weight. Later experiments allowed analysis of the coupling reactions results, and I will return to this subject.

It was desirable to functionalize the endgroups of these polymers, and Fig. 3 shows a successful route to incorporate hydroxyl groups. The known lithium compound shown on the right reacted cleanly with

TABLE 1. Stoichiometric sec-BuLi + Pyridine in Tetrahydrofuran, -78° C

Py/RLi	M/I (theory DP)	Monomer addition rate	Product GPC $\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	DP actual
1	80	Slow	6,400	6,200	0.96	62
1	80	Rapid	31,000	43,000	1.41	310
10	80	Slow	6,400	6,400	1.00	64
10	80	Rapid	12,000	13,000	1.09	120
10 (-20° C)	80	Rapid	9,000	11,000	1.26	90
2 (-20° C)	80	Slow	6,100	17,000	2.80	61
2 (-20° C)	80	Rapid	9,300	13,000	1.43	93
10 (n-BuLi)	80	Rapid	38,000	258,000	6.85	380

TABLE 2. 1,1-Diphenylethylene Initiator:



$$n\text{-}C_4H_9Li + CH_2{=}C(C_6H_5)_2 \xrightarrow[RT]{THF} n\text{-}C_5H_{11}C^{\ominus}(C_6H_5)_2\,Li^{\oplus}$$

DPHLi

(cf. D. M. Wiles and S. Bywater, 1964)

$$\text{DPHLi} + n\text{MMA} \xrightarrow[-78^\circ C]{THF} \text{DPH}\!\left(\!\text{MMA}\right)_n^{\ominus}$$

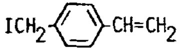
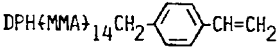
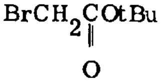
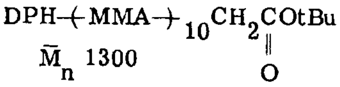
M/I (theory DP)	GPC $\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	DP actual
15	1,500	1,400	0.90	15
30	3,000	2,700	0.89	30
62	6,300	6,000	0.97	63
125	14,000	15,000	1.03	140
250	25,000	27,000	1.10	250
500	102,000	274,000	2.69	1,020

TABLE 3. Block Copolymers: Lauryl Methacrylate (LMA) and Methyl Methacrylate (MMA)

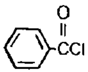
	$\bar{M}_w/\bar{M}_n$	T_g's
DPH $(MMA)_{200}$-b-$(LMA)_{67}$	1.31	-5°C, 105°C
DPH $(MMA)_{200}$-b-$(LMA)_{134}$	1.72	-44°C, -5°C, 105°C
DPH $(MMA)_{200}$-b-$(LMA)_{200}$-b-$(MMA)_{200}$	3.56	-44°C, -5°C, 105°C

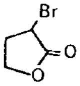
TABLE 4. Capping Reactions of the PMMA Anion

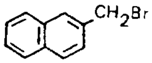
$$\mathrm{DPH{+}(MMA)_n^{\ominus} + RX \longrightarrow DPH{+}(MMA{+})_nR + LiX}$$

Capping agent	Product	NMR (UV)
	 $\bar{M}_n$ 1700	Vinyl; δ 5.10, 5.25, 5.50, 580 ($k_{252nm} = 7.82$) (92% reaction)
$\mathrm{BrCH_2CH{=}CH_2}$	$\mathrm{DPH{+}(MMA{+})_{10}CH_2CH{=}CH_2}$ $\bar{M}_n$ 1300	Vinyl; δ 4.80, 4.96, 5.12, 5.42, 5.55 Aromatic to vinyl 10:3
 $\mathrm{BrCH_2\underset{\underset{O}{\|}}{C}OtBu}$	 $\mathrm{DPH{+}(MMA{+})_{10}CH_2\underset{\underset{O}{\|}}{C}OtBu}$ $\bar{M}_n$ 1300	tBu; δ 1.42 Aromatic to t-butyl 10:12

Others:







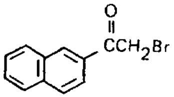
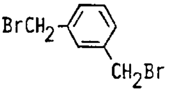
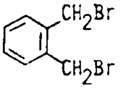


TABLE 5. Coupling the PMMA Anion:

$$2\mathrm{In}\text{-}(\mathrm{MMA})_n^{\ominus} + \mathrm{X{-}R{-}X} \xrightarrow{-78^\circ\mathrm{C}} \mathrm{In}\text{-}(\mathrm{MMA})_n\text{-}\mathrm{R}\text{-}(\mathrm{MMA})_n\text{-}\mathrm{In} + 2\mathrm{LiX}$$

Py/s-BuLi Initiator

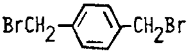
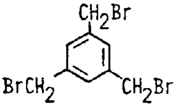
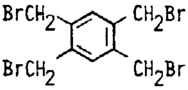
	GPC				
	Control		Product		
Coupling agent	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	% Coupling
	5,800	0.99	11,000	1.08	95
	1,600	1.22	3,200	1.63	100
	1,500	1.07	2,600	1.57	85
 (After MeOH)	1,200	1.29	1,200	1.39	0

1,1-diphenyl ethylene to provide a diphenyl pentyl lithium initiator with a protected hydroxyl group. Polymerization occurred normally and on treatment of the anion with strong acid, hydroxyl-terminated polymers were obtained. With protonation by methanol, polymer with the acetal endgroup could be obtained.

High pressure liquid chromatography proved very informative in this system. Figure 4 shows the polymer with acetal endgroups at the bottom and hydrolyzed at the top. For identification purposes, samples of hydroxyl polymer were isolated and characterized by NMR, analysis, etc. This kind of separation of acetal from hydroxyl ended polymer turned out to be general for all the examples studied. As will be seen later, this method allowed us to study the capping and coupling reactions quantitatively.

The separation was practical at MW's up to 10,000 as shown in Fig. 5. The UV detector confirmed that DPPH moiety is present in all fractions.

TABLE 6. Coupling: DPHLi Initiator

	GPC				
	Control		Product		
Coupling agent	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	% Coupling
	1,000	1.10	1,800	1.06	89
Ditto, 0°C	1,400	1.00	1,500	1.00	13?
	900	1.28	1,600	1.43	
	1,000	1.20	2,100	1.40	
$I(CH_2)_4I$	1,400	1.20	2,100	1.24	67

Hydroxyl polymers could also be prepared using an allyl-containing initiator followed by hydroboration. The "other end" of the polymer could be functionalized by capping the PMMA anion with allyl bromide followed by hydroboration (Fig. 6). Once again, HPLC confirmed the hydroxylation and allowed quantitative analysis of the reaction (Fig. 7). This hydroboration chemistry can provide terminally difunctional polymers as does coupling of the acetal-ended polymer. As shown in Fig. 8, the acetal-capped anion reacted smoothly with p-xylylene dibromide to couple the anions, and the product was hydrolyzed to the dihydroxy polymer (Fig. 9). As prepared, products were about 90% difunctional, as shown by HPLC, and pure samples for characterization and chain extension studies were easily isolated.

This technique provided the basis for studying the coupling reaction, as shown in Fig. 10. Yields of slightly over 90% could be obtained, but the cyclization reaction prevented finishing the reaction by heating. The data were obtained by removing aliquots, protonating, and analyzing by the HPLC technique. We were not successful in finding a quantitative coupling reaction needed to provide 100% terminally difunctional material, directly.

The same techniques could be used to study coupling with multifunc-

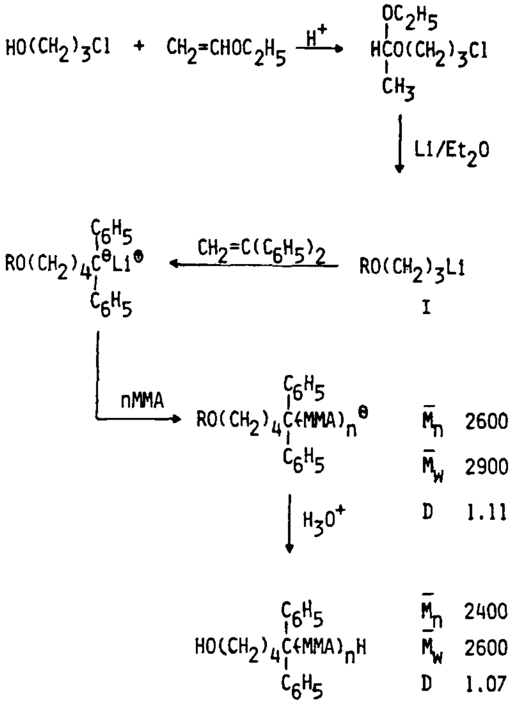


FIG. 3. Functional initiators.

tional compounds as mentioned earlier. The reactions in Fig. 11 were studied briefly to evaluate this method of synthesizing tri- and tetrafunctional polymers. Figure 12 shows the results. From tris (bromomethyl) benzene, di- and trifunctional species were obtained, and from tetrakis (bromomethyl) benzene, di-, tri-, and tetrafunctional species. Chromatographic separations of the trifunctional polymer from tris bromomethyl benzene and the tetrafunctional polymer from tetrakis bromomethyl benzene were easily accomplished, and these materials were characterized. Because of the low yields, they were not extensively studied.

At this stage we were very familiar with the anionic system and decided to use it to prepare a series of air reactive methacrylate polymers by anionic polymerization of diene containing esters of methacrylic acid. Wiles and Brownstein (1965) and D'Alelio and Hoffend (1967) showed that allyl methacrylate could be polymerized in this way, but no literature references to direct preparation of diene-containing esters were found (Fig. 13). Gerry Andrews made the series of esters shown in Table 7 by conventional synthesis of

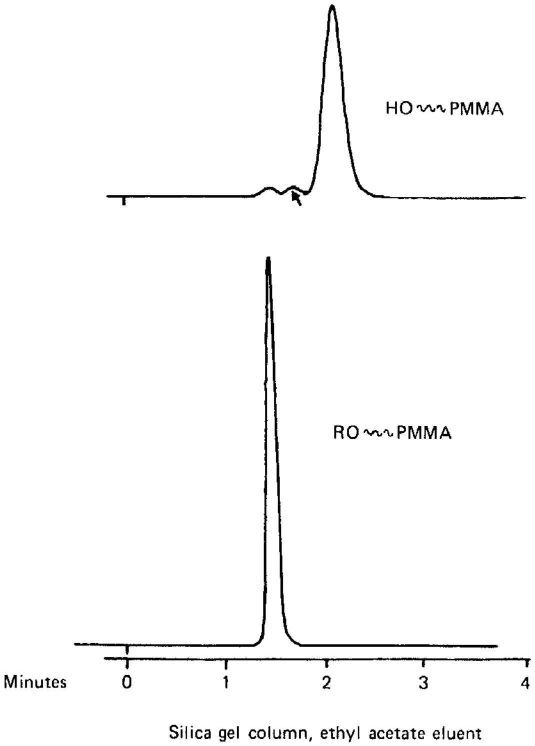


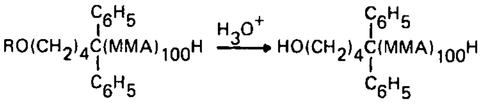
FIG. 4. HPLC separation of acetal- and hydroxyl-ended PMMA.

the dienols followed by transesterification. Polymerization was accomplished under conditions shown in Table 8. It is interesting that the conditions led to no rearrangement of the dienes.

Polymers were obtained in the desired molecular weight range and all were quite reactive with air. Gel permeation chromatography gave slightly broadened MWD's, perhaps due to cross-linking during handling. All the products were soluble and most could be formulated into coatings, which air dried in the expected way. The cyclohexadiene containing polymers were exceptions—oxidation led to aromatization of the rings.

Coatings from these materials had the expected stability in air; many were better than typical drying-oil formulations. Table 9 shows a group of typical compositions made this way.

To summarize—conditions have been found for anionic polymerization of methyl methacrylate which avoid termination and transfer reactions resulting in precise control of molecular weight (Fig. 14). Molecular weight distributions can be very narrow. Procedures for



$$RO(CH_2)_4\overset{C_6H_5}{\underset{C_6H_5}{C}}(MMA)_{100}H \xrightarrow{H_3O^+} HO(CH_2)_4\overset{C_6H_5}{\underset{C_6H_5}{C}}(MMA)_{100}H$$

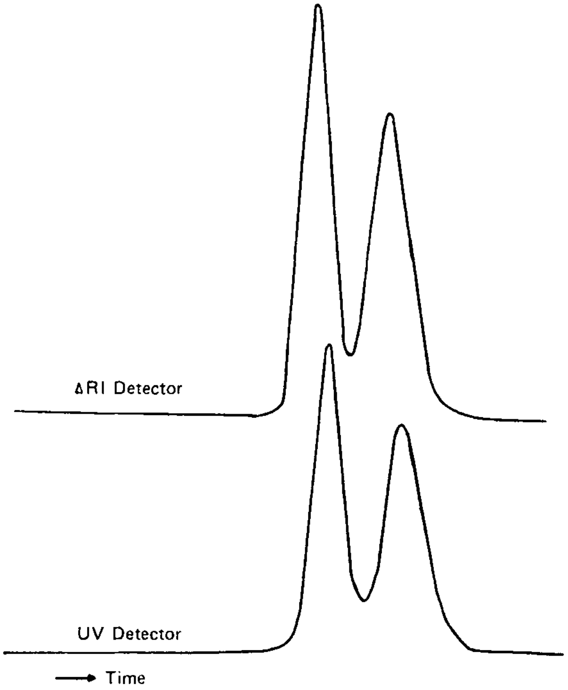


FIG. 5. HPLC separation of hydrolyzed acetal polymer.

functionalizing chain ends and coupling living anions have been described. Copolymers and block polymers can be made at very high conversion. The system is limited to methacrylates at -78°C to, in some cases, -20°C by cyclization of the growing anion. Acrylates cannot be included because the polymer is a chain terminator.

In the last few minutes I have, I'd like to tell you about some further chromatographic experiments. The separations I have described are remarkable when we consider that a polymer of DP-10 made by ionic polymerization has significant amounts of oligomers from DP = 4 all the way up to DP = 16. The key to this separation is that the ethyl acetate eluent is polar enough to overcome the absorption of all of the ester groups into the silica gel and allow the polarity of the endgroups to influence the retention time of the material (Fig. 15).

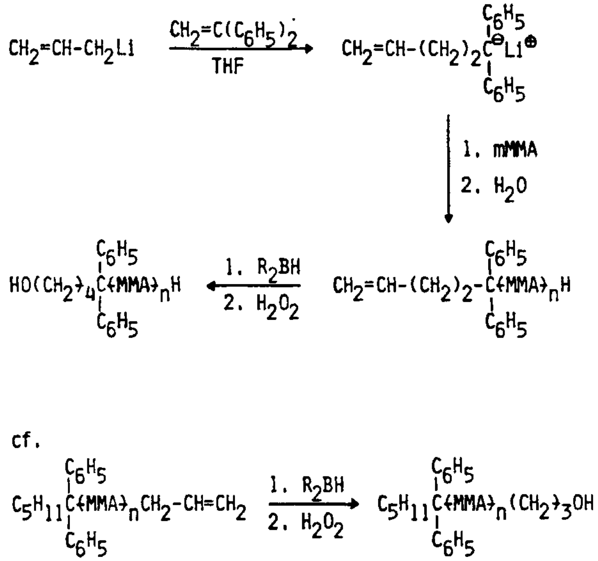


FIG. 6. Functional initiators.

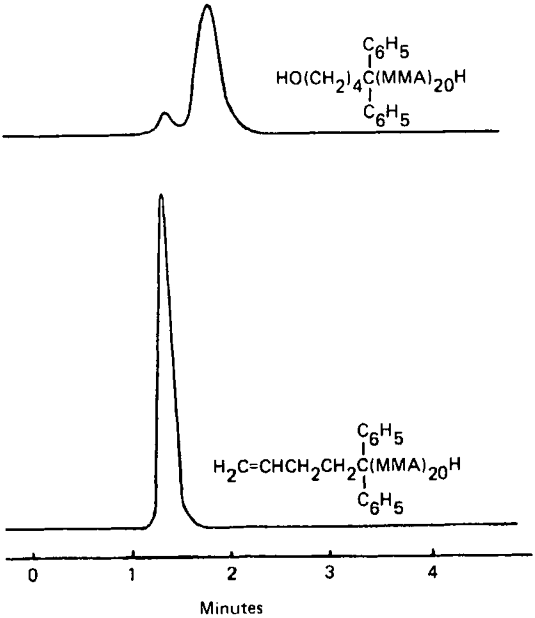


FIG. 7. HPLC separation of hydroboration product.

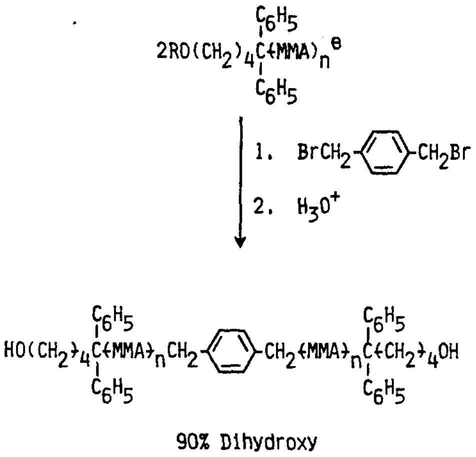


FIG. 8. Coupling and hydrolysis of the acetal PMMA anion.

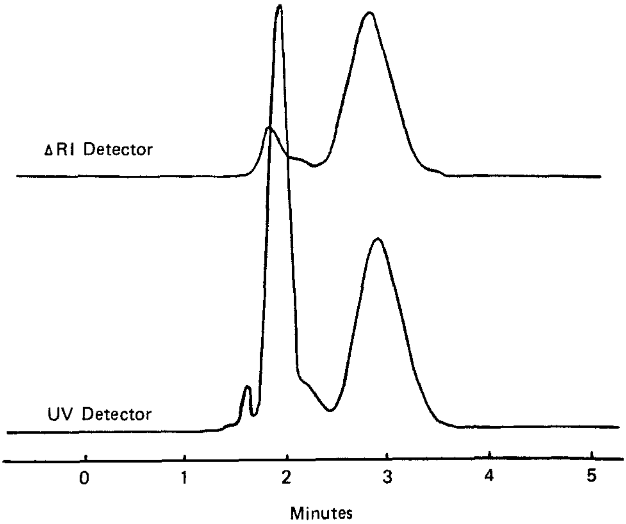


FIG. 9. HPLC separation of hydrolyzed product from dibromo-p-xylene coupling.

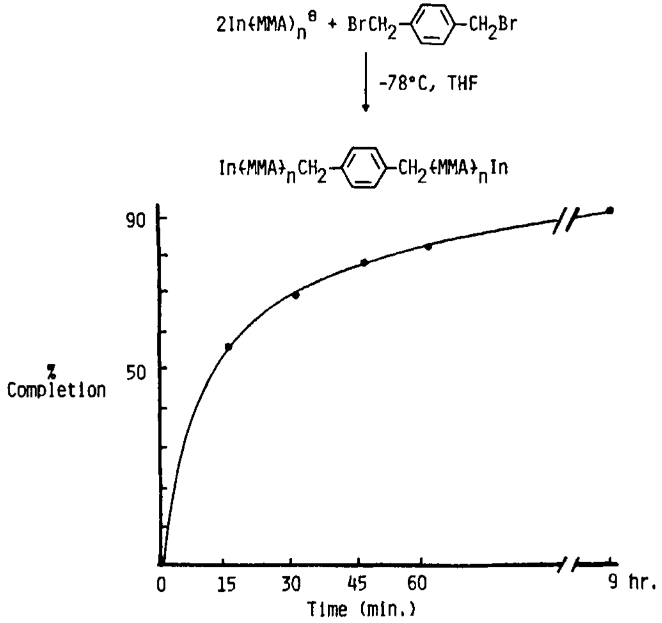


FIG. 10. Rate of coupling.

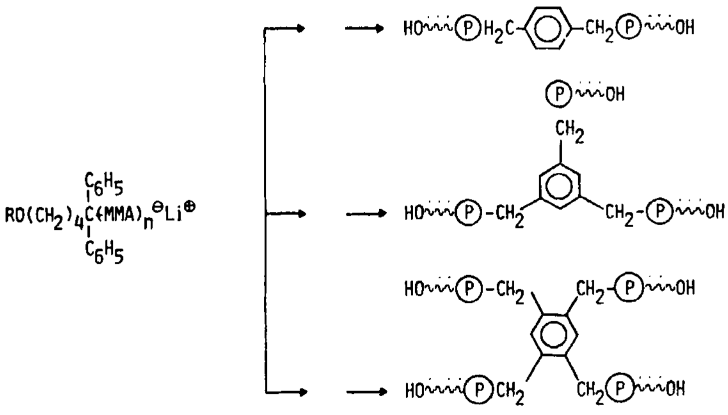


FIG. 11. Coupling with poly(bromomethyl) benzenes.

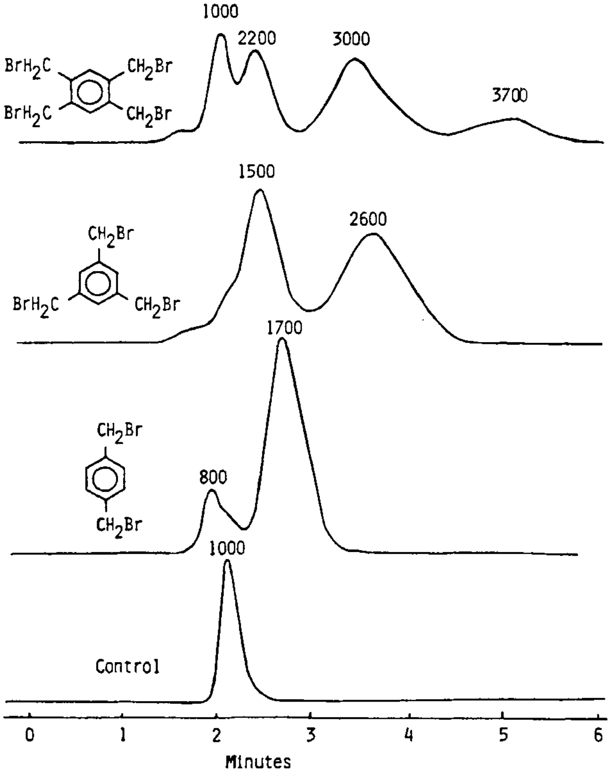
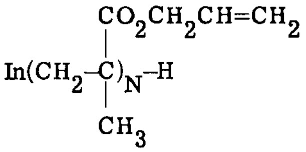


FIG. 12. HPLC separation of polyols from coupling of living PMMA with poly(bromomethyl) benzenes.



$$\mathrm{In}(\mathrm{CH_2}-\overset{\overset{\textstyle \mathrm{CO_2CH_2CH{=}CH_2}}{|}}{\underset{\underset{\textstyle \mathrm{CH_3}}{|}}{\mathrm{C}}})_N-\mathrm{H}$$

FIG. 13. Poly(allyl methacrylate).

TABLE 7. Dienyl Methacrylates Prepared by Transesterification of the Corresponding Alcohol

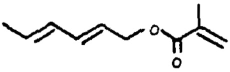
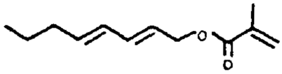
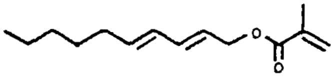
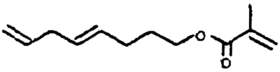
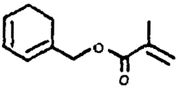
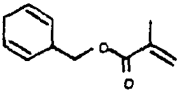
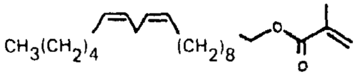
Methacrylate	Structure	Yield (%)
2,4-Hexadienyl		71
2,4-Octadienyl		78
2,4-Decadienyl		65
4,7-Octadienyl		87
1,3-Cyclohexadienylmethyl		72
2,5-Cyclohexadienylmethyl		87
9,12-Octadecadienyl		~100

TABLE 8. Dienyl Methacrylate Copolymers

Conditions:

Diphenylhexyllithium initiator
THF solution, -78°C, 20% solution, 50 g scale
5-100% Dienyl methacrylate
Remainder butyl and/or methyl methacrylate

Polymers:

MW 1,000-16,000
$\bar{M}_w/\bar{M}_n$ 1.2 to 1.8
Yields ~100%
NMR confirms compositions
Polymers cross-link readily in air
Cross-linked films show expected stability

TABLE 9. Dienyl Methacrylate Polymer and Copolymers Prepared as Described in Text

	Monomer (mol%)		DP		$\overline{M}_n$	$\overline{M}_w$	
Methacrylates	Feed	Polymer	Calc	Obs	$\frac{\overline{M}_n}{1000}$	$\frac{\overline{M}_w}{\overline{M}_n}$	T_g (°C)
2,4-Hexadienyl	100	100	10	12	1.5	1.8	-
2,4-Hexadienyl	15	15					
Butyl	57	53	100	94	13	1.1	23
Methyl	28	32					
2,4-Octadienyl	15	15					
Butyl	53	54	110	136	16	1.6	39
Methyl	32	30					
2,4-Decadienyl	15	16					
Butyl	34	38	110	109	15	1.4	42
Methyl	51	47					
4,7-Octadienyl	15	17					
Butyl	53	54	110	106	13	1.4	31
Methyl	32	29					
1,3-Cyclohexadienylmethyl	15	16					
Butyl	53	55	110	121	13	1.5	47
Methyl	32	29					
2,5-Cyclohexadienylmethyl	15	13					
Butyl	53	55	110	149	19	1.7	54
Methyl	32	31					

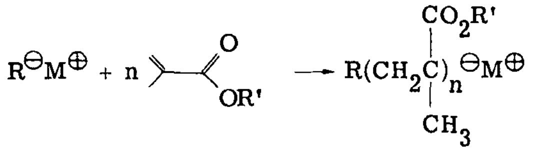
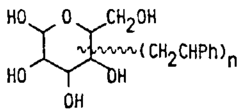


FIG. 14. Anionic polymerization: No termination or transfer, controlled molecular weight, narrow MW distribution, functionality at chain ends, and block copolymers.

$HO\sim\sim(CH_2CH{=}CHCH_2)_n\sim\sim OH$

H. Inagaki, 1977



T. I. Min and H. Inagaki, 1980

$In(CH_2CHPh)_nCO_2H$

P. Månsson, 1980

FIG. 15. Separations of other functional polymers.

We always wanted to see what would happen if we tried to separate the individual oligomers of these polymers. Figure 16 shows a chromatogram of a low molecular weight, DP-5 polymethyl methacrylate made especially for this analysis. The chromatogram is run on the same silica gel column that is used for the other separations that I have shown in the previous illustrations. This material is eluted with a gradient starting at the injection point with pure butyl chloride, a nonpolar solvent, and increasing linearly in the amount of acetonitrile up to 20% at 20 min. The detector here is a UV detector which detects the phenyl groups at the end of each polymer chain. At first we didn't understand why there were two peaks for each oligomer. Samples of these oligomers were isolated; that is, fractions 1, 2, and 3 were collected and the individual peaks analyzed by NMR. This showed that the peak marked 1 is the oligomer with DP = 1. Each of the peaks marked 2 is an oligomer with DP = 2 and each of the peaks marked 3 is an

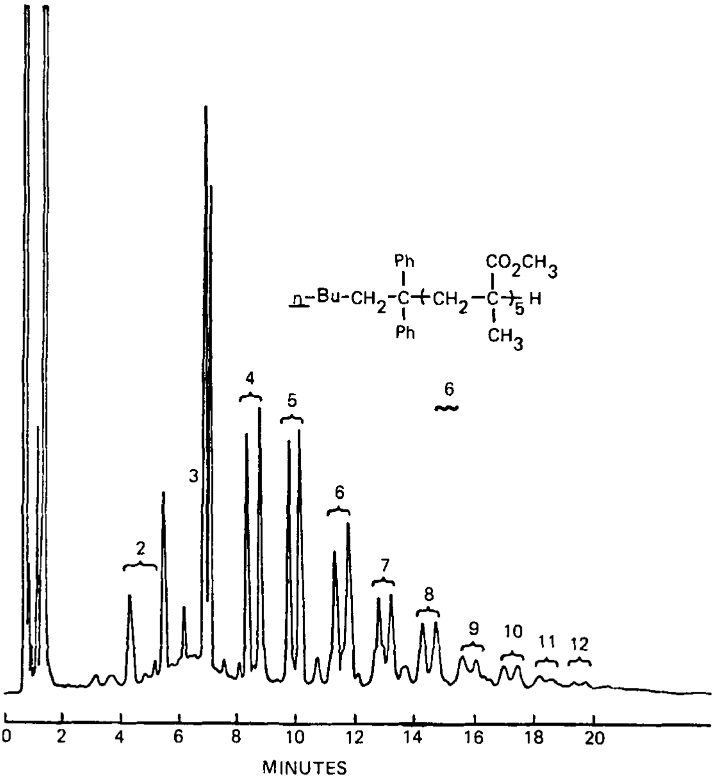


FIG. 16. HPLC separation of PMMA oligomers with chiral termini.

oligomer with DP = 3. The reason that there are two peaks for each oligomer has to do with stereochemistry of the last two units on the chain. Each of those units has an asymmetric center and there are two isomers with different configurations of the two units.

We can demonstrate this fact by instead of quenching the polymer with water, quenching it with methyliodide which methylates the end-group and eliminates one of the asymmetric centers in the polymer. Figure 17 is a chromatogram of this material under exactly the same conditions as that of Fig. 16. As you can see, there is now only one peak for each oligomer. As I said before, the stereochemistry of these polymers is predominantly syndiotactic and the stereoselectivity is such that the chance that any two units are in a syndiotactic arrangement is about 90%. We can see in these later peaks starting around DP-5 that there is in fact a shoulder in each one of the peaks which is approximately 10% of the area of the bigger peak. This indicates that

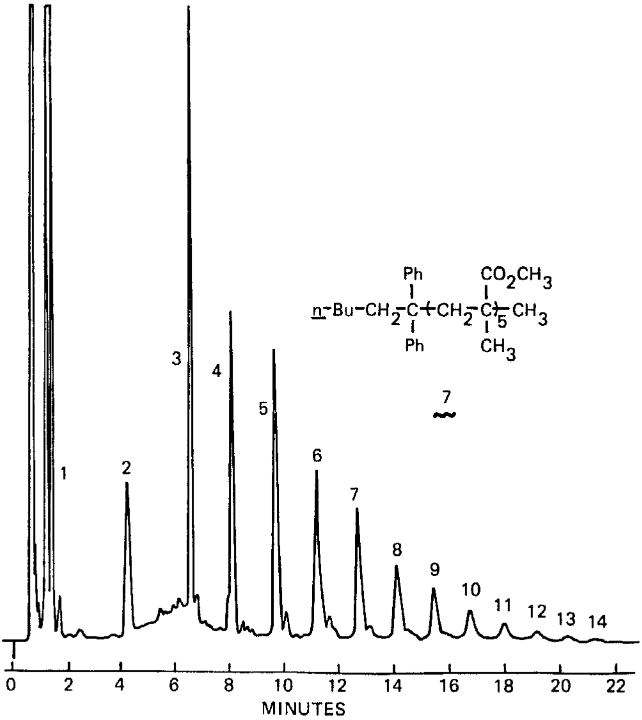


FIG. 17. HPLC separation of PMMA oligomers with achiral termini.

in fact we can separate even farther down the polymer chain. It also explains why the separations get more and more difficult as the molecular weight increases because the number of isomers increases astronomically and in fact for an oligomer with DP = 10 there are 512 possible isomers. Oligomer separations such as these have also been reported in the literature, but no polymer with the stereochemical complexity of polymethyl methacrylate has been analyzed. We have extended this oligomer separation to the separation of the oligomers of polyethers and polyesters, and this separation technique promises to be a very powerful method for the analysis of low molecular weight polymers.

ACKNOWLEDGMENTS

Gerry Andrews did much of the functional initiator and diene polymer work, as well as much of the chromatography. Paul Arthur

studied the butyllithium pyridine system and first observed polymers with narrow MWD's. Jake Jacobson scoped much of the capping chemistry and started the DPHLi work. Russ Melby made copolymers and block copolymers, and did many capping studies. C. H. Park optimized the coupling reactions. Tony Playtis made and studied highly syndiotactic methacrylate polymers. Bill Sharkey supervised much of the work. Art Vatvars contributed to the chromatographic experiments. Finally, I'd like to thank Bob Lipscomb for much of the detailed data about Speed Marvel's long relationship with DuPont.