Telechelic Elastomers

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Synopsis

Telechelic elastomers, polymers with reactive terminal groups, can be prepared in emulsion and solution systems. Examples of characterization of the polymers and preparation of a mercapto telechelic copolymer in an emulsion system and of mercapto-, hydroxy-, and aziridinyl-telechelic elastomers in solution systems are given. The elastomers were cured in peroxide or sulfur–accelerator formulations. The telechelic polymers exhibited enhanced stress–strain and dynamic properties in comparison to those of the controls. In tread formulations, outstanding properties were obtained for the mercapto- and aziridinyl-telechelic butadiene–styrene copolymers.

INTRODUCTION

Preparation of telechelic polymers (Greek *telos*, end, plus *chele*, claw), i.e., polymers possessing two reactive terminal groups, by an emulsion and a solution procedure was previously described.[1] The solution procedure is being used in the commercial production of a liquid carboxy-telechelic polybutadiene, Butarez CTL (Phillips Petroleum Co.), and a hydroxy-telechelic polybutadiene, Butarez HT. Some of the physical properties,[2-4] production details,[5] and uses, as in rocket binders,[6] of these hydrocarbon polymers have been described.

The present report covers an extension of the procedures described[1] for the preparation of solid elastomeric products. One of the reasons for preparing these reactive polymers was to provide a means for incorporating the polymer chain ends into a vulcanizate network. This should result in more efficient utilization of the polymer molecules and in superior physical properties.[7,8]

The prerequisite for a high degree of incorporation of chain ends is a high telechelicity. Since the useful range of molecular weights for solid elastomeric polymers is a $\bar{M}_n$ of 5–200 $\times$ 10^4, the concentration of end groups in these polymers is frequently too low to detect analytically. When conventional analyses are inapplicable, several other means of establishing telechelicity are available. One such procedure is to prepare a liquid telechelic polymer, analyze by a conventional method for end groups, determine efficiency of endgroup attachment, and then assume the same efficiency holds for the preparation of the higher molecular weight polymer. Another indirect means of establishing telechelicity is to measure solution

viscosity before and after a coupling reaction, and then calculate telechelicity by known relationships. This usually gives a lower limit of telechelicity because of the difficulty of getting quantitative coupling. Finally, a comparison of the control and experimental polymer raw and vulcanizate properties also offers evidence for the presence of terminal groups in the polymer molecules.

The following reports the preparation, characterization, and vulcanization of telechelic elastomers.

EXPERIMENTAL RESULTS

In the following sections, the preparations and characterizations will be presented in detail when this information does not already exist in the literature.   In the latter cases, literature references will be largely relied on.

Mercapto-Telechelic Butadiene-Styrene Copolymer Prepared in Latex

Diisopropylxanthogen disulfide (Dixie) was one of the first sulfur-containing compounds used as a modifier in the emulsion polymerization of dienes.[9] The use of Dixie to prepare xanthate-telechelic polymers and the hydrolysis to mercapto-telechelic groups has never been described in any detail in the literature.   The following are laboratory and practical procedures for preparing mercapto-telechelic polymers.

For studying the hydrolysis, a liquid polymer containing a relatively large amount of xanthate groups is useful. Although Dixie is a troublesome retarder, emulsion polymerization of butadiene in the presence of 5–7 parts of the disulfide can be accomplished readily by using the sulfoxylate recipe at 30°C or employing higher levels of the initiator at 5°C. Typical data for the polymerization of butadiene in the presence of 5 parts of Dixie are shown in Table I.

For a polymer of normal Mooney viscosity, 60% conversion could be attained in 6 hr by using 0.4 parts of Dixie with p-menthane hydroperoxide

TABLE I
Rate Data for Preparing Xanthate-Telechelic Polybutadiene at 30°C[a]

PMHP phm	FeSO$_4$. 7H$_2$O, phm	Questex, phm	Na formaldehyde sulfoxylate (SFS), phm	Conversion, %				
				3.5 hr	4.5 hr	6.0 hr	11 hr	23 hr
0.1	0.018	0.058	0.045	15	18	22	23	25
0.2	0.018	0.058	0.090	17	32	41	71	—
0.3	0.018	0.058	0.135	40	52	80	—	—
0.3	0.018	0.058	0.045	18	22	23	30	52
0.2	0.036	0.116	0.090	26	26	28	28	29

[a] Nonvariable recipe: butadiene, 100 parts; water, 180 phm (parts per 100 parts monomer); K fatty acid soap, 5.0 phm; KCl, 0.5 phm; Dixie, 5.0 phm.

(PMHP) at the 0.2 level and the activator content adjusted proportionately. Incremental addition of Dixie was employed when conversions higher than 60% were attained.

Hydrolysis was most efficaciously accomplished in hydrocarbon solution with hydrazine as a catalyst. For practical purposes hydrolysis was carried out in latex with ammonium hydroxide or ethylenediamine as catalyst. Kinetic studies in latex showed that the hydrolysis reaction was pseudo first-order with respect to the xanthate. The rate constant varied linearly from 0.059 to 0.216 hr^{-1} as the ammonia was increased from 5.0 to 20 phr at 70°C. Typical rate curves for hydrolysis of a liquid polymer in latex with ammonia and ethylene diamine as catalysts are shown in Figure 1. The mercaptyl groups generated were determined by the silver nitrate amperometric titration procedure.[10,11]

The curve for hydrolysis with the diamine shows a decrease after 2 hr. This decrease corresponds with that observed if the latex is destabilized during hydrolysis. The rate constant for hydrolysis with the high concentration of ammonia is about 25% lower than might be expected if the linear relationship at lower concentration were extrapolated. Such a deviation might not be unexpected in view of the complexity of the system studied.

Besides the chemical proof obtained by the silver nitrate amperometric titration for mercapto group found during hydrolysis, the polymer showed a split 7.75 μ band which is characteristic of the isopropyl group and also four bands were observed in the 8–10 μ regions uncommon to polybutadiene but known for alkyl ethers. The presence of similar bands for a xanthate-telechelic polystyrene have been reported by others.[12] After hydrolysis, the 7.75 μ split band and the four bands just mentioned were absent. Chemical analyses for sulfur are also consistent with the presence of xan-
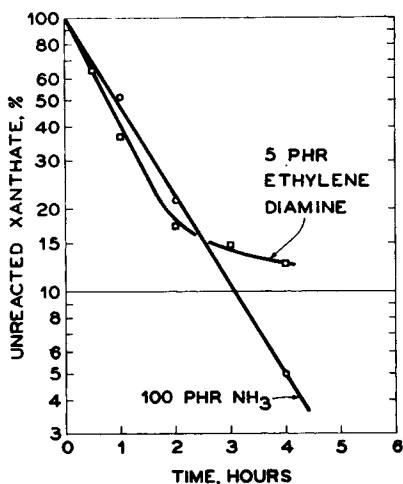

Fig. 1. Hydrolysis of a liquid xanthate-telechelic polybutadiene in latex with ethylenediamine and ammonium hydroxide at 70°C.

TABLE II
Polymerization and Characterization Data of Telechelic
Polymers Prepared for Evaluation

	Xanthate-telechelic	Control
Polymerization		
Butadiene/styrene	72/28	72/28
Modifier and amount, phm	Dixie, 0.4	Sulfole, 0.3
Temperature of polymerization, °C	5	5
Conversion, %	78	65
Time, hr	15.5	4.9
Original polymer		
Inherent viscosity, dl/g	1.52	1.47
Sulfur, %	0.24	0.09
Molecular weight	89,000[a] or 53,000[b]	
After hydrolysis		
Inherent viscosity, dl/g	1.84 (35 ML-4)	—
Mercaptan, meq phr	5.5	—
Sulfur, %	0.15	—

[a] $[\eta] = 2.95 \times 10^{-4} \bar{M}_n^{0.75}$ (Relation used by Vaclavek,[18] and developed by Chinese authors.[14]

[b] Assuming two xanthate groups per polymer molecule.

thate group before hydrolysis and with the presence of mercaptide groups after hydrolysis.

For some evaluation studies a Dixie and a Sulfole mercaptan-modified 72/28 butadiene–styrene copolymer were prepared to the same inherent viscosity at 5°C in a sulfoxylate recipe at a 0.08 PMHP level. Some polymerization and characterization data are given in Table II.

The xanthate-telechelic polymer, the mercapto-telechelic polymer, the laboratory control, and SBR 1500 were compared in various curing formulations. The stocks were mill-mixed by the standard procedure. Results for peroxide-cured polymers are given in Table III.

Vulcanization of the mercapto-telechelic copolymer in a standard tread recipe resulted in an overcured stock. Further compounding work was also tried at reduced curative levels (Table IV).

Table IV shows that only a small amount of accelerator is necessary to cure the mercapto-telechelic polymer satisfactorily. During the evaluation the mercapto-telechelic formulation began to set up or toughen at room temperature after addition of the curatives. Tensile slabs displayed a slight roughness, which indicated the stock did not flow properly into the mold or was scorching prior to application of pressure. The mercapto-telechelic polymer was at a low state of cure as judged by modulus and crosslinking data; however physical properties were quite good. The tensile and resilience were noteworthy in comparison to the laboratory control even though very small amounts of accelerator were employed in the experi-

TABLE III
Peroxide Cure of Telechelic Polymers[a]

Physical properties	Mercapto-telechelic polymer	Xanthate-telechelic polymer	Sulfole polymer	SBR 1500
300% Modulus, psi	3550	2450	1150	2400
Tensile, psi	4500	3050	2500	3050
Elongation, %	380	360	570	400

[a] Compound recipe: 100 parts polymer, 50 phr Philback 0, 2.5 phr DiCup 40 C. Cure: 30 min at 153°C.

TABLE IV
Emulsion Mercapto-Telechelic Polymer Compounded
at Reduced Curative Levels[a]

Physical properties	Mercapto polymer	Mercapto polymer	Xanthate polymer	Sulfole polymer	SBR 1500[b]
Santocure, phr	0.15	0.2	0.75	1.2	1.2
Cure 45 min at 1530					
$\nu \times 10^4$, mole/cc	0.79	1.07	1.44	1.23	1.52
Compression set, %[c]	25	23	26	19	20
Modulus, 300%, psi	700	1100	1500	1500	1500
Tensile, psi	2600	3700	3260	3100	3900
Elongation, %	610	600	510	510	590
Tear resistance, lb/in.	295	220	250	355	220
ΔT, °F	99	81	82	80	61
Resilience, %	65	67	60	57	62
Shore hardness[c]	64	66	63	61	58
Oven-aged 24 hr at 100°C					
Modulus, 300%, psi	1300	1700	2600	2200	2170
Tensile, psi	3300	3700	3400	3500	3200
Elongation, %	560	490	350	410	410
ΔT, °F[c]	81	68	68	68	52
Resilience, %[c]	68	71	67	64	67

[a] Polymer, 100 parts; Philblack 0, 50 phm; ZnO, 3 phr; stearic acid, 2 phr; Flexamine, 1 phr; sulfur, 1.75 phr.

[b] 1.0 phr stearic acid and 10 phr Philrich 5 used in this mix.

[c] 30 min. cure.

mental polymers. Retention of stress strain properties after aging of the experimental stock was also good.

Coupling Lithium-Telechelic Polybutadiene

Telechelicity refers to the fraction of polymer ends possessing functional groups. One simple means of estimating the telechelicity of organolithium initiated polymers is to measure the viscosity of the isolated polymers before

TABLE V

Coupling of Lithium-Telechelic and of Lithium-Semitelechelic Polybutadiene with Bis(Chloromethyl) Ether

Organo Li, mMHM[a]	Initial molecular weight data			Molecular weight after coupling				
	η_{inh}	M_k[b]	$\bar{M}_{kv}$°	η_{inh}	$2 \times M_k$	$\bar{M}_{kv}$°	n[d]	tl
				Lithium semi-telechelic polybutadiene				
2.0	0.83	50,000	46,000	1.27	100,000	89,000	1.84	0.43
4.0	0.57	25,000	26,000	0.82	50,000	45,000	1.54	0.36
15.0	0.27	6,700	8,200	0.42	11,400	16,000	1.80	0.45
				Lithium-telechelic polybutadiene				
4.0[e]	0.73	25,000	38,000	6.09		10^6	26.3[f]	0.96[g]
10.0[e]	0.28	10,000	8,700	1.95		170,000	19.5[f]	0.95[g]

[a] In mmole/100 g monomer.

[b] Grams butadiene polymerized)/(mole of effective initiator).

[c] $[\eta] = 7.76 \times 10^{-4} M_k^{0.65}$. (Relationship of Zelinski and Wofford.[16])

[d] ($\bar{M}_n$ coupled polymers)/(M_n primary polymer) = n where n is the number-average degree of coupling. See text for derivation.

[e] Dilithiumstilbene initiator.

[f] ($\bar{M}_{kv}$ coupled)/($\bar{M}_{kv}$ primary polymer) = n'.

[g] $(n' - 1)/n' = tl'$.

and after subjecting the active polymer in solution to a coupling reaction and then calculating the results on the basis of known relationships.

A lithium-semitelechelic polybutadiene was prepared by polymerizing butadiene by means of n-butyllithium, and a lithium-telechelic polybutadiene was prepared by initiating the polymerization with a dilithiumorgano compound. Allowances were made for impurities, and polymerizations were conducted by procedures previously described.[15] A portion of each polymerization solution was terminated with alcohol and another portion was treated with a stoichiometric amount of bis(chloromethyl) ether as a coupling agent. The inherent viscosity η_{inh}, the kinetic molecular weight M_k, the viscosity-average kinetic molecular weight $\bar{M}_{kv}$, the number-average degree of coupling n, and the telechelicity t_1 [$= (n-1)/n$] for the two series of polymerizations are presented in Table V.

One of the chief values of the data in Table V is to provide a measure of the fraction of chain ends that possess a lithium ion. The theoretical tl for a telechelic polymer is 1.0 and that for the semitelechelic polymer is 0.5. The experimental data for the semitelechelic polymer show that from 72 to 90% of the theoretical telechelicity had been attained. This type of lithium-telechelic polymer should be excellent for preparing polymers with curable end groups provided that reactive reagents and proper experimental conditions are used. The preparation of telechelic polymers by means of dilithiumorgano initiators under the conditions just used follow.

Mercapto-Telechelic Butadiene–Styrene Copolymer Prepared in Solution

The procedure described above was employed to prepare a lithium-telechelic polymer in solution which was reacted with sulfur to give a mercapto-telechelic butadiene-styrene copolymer. Details and variations of the steps used have also been published,[17] and the specific recipe and experimental data are presented in Table VI.

Preliminary vulcanization tests showed the mercapto-telechelic polymers were overcured with a standard tread type recipe. Better balance of properties was obtained at lower accelerator levels, as was the case for the

TABLE VI
Preparation of Mercapto-Telechelic Butadiene–Styrene Random Copolymer[a]

| Li₂R, mMHM | Sulfur added | | Polymer analysis | | Viscosity | |
	Parts	mMHM	Mercapto, mMHM	Sulfur, mMHM[b]	η_{inh}	ML-4
1.8	0.106	3.3	0.45	2.2	2.63	52
2.0	0.115	3.6	0.45	2.5	2.78	48
1.1	—[c]	—	—	—	1.8	53

[a] Polymerization recipe: butadiene/styrene, 77/23 parts; cyclohexane, 1200 phm; tetrahydrofuran, 1.5 phm; dilithiumstilbene initiator, 1.8 or 2.0 mmole/100 monomer (mMHM); 50°C.; 2.0 hr: 100% conversion.

[b] Sulfur analysis by the Leco Sulfur procedure.

[c] Control polymer.

TABLE VII
Solution Mercapto-Telechelic Copolymer Compound in a Tread Formulation

	Mercapto polymer[a]	Mercapto polymer[a]	Control	SBR 1500	SBR 1500
Variable compounding ingredients, phr[b]					
Stearic acid	2	2	2	1	1
Philrich 5	—	—	—	—	10
Santocure	0.6	0.6	0.8	0.8	1.2
Cured 30 min at 153°C					
Compression set, %	24.3	25.5	21.0	27.9	21.3
300% modulus, psi	3100	2300	1800	1600	1400
Tensile, psi	4200	4300	3900	3800	4100
Elongation, %	500	490	510	600	620
ΔT, °F	58	58	64	87	67
Resilience, %	70	70	68	58	61
Permanent set, %	1.9	1.6	1.8	7.2	2.7
Shore A hardness	68	67	71	63	61
Aged 24 hr at 100°C					
300% modulus, psi	3000	3200	2600	3000	3200
Tensile, psi	3500	3800	3100	3900	3800
Elongation, %	340	340	330	380	470
ΔT, °F	46	47	54	59	54
Resilience, %	75	74	73	65	66
Permanent set, %	0.5	0.4	0.3	0.7	0.5

[a] Polymer preparation given in Table VI.

[b] Ingredients common to the formulation: polymer, 100 parts; Philblack 0, 50 phr; ZnO, 3.0 phr; Flexamine, 1.0 phr; sulfur, 1.75 phr.

polymers prepared in the emulsion system. Typical evaluation data showing formulation variables needed to obtain reasonable cures and good physical properties are presented in Table VII.

In addition to the accelerator level, other evidence that the mercapto-telechelic polymers had different cure characteristics were scorch times that were 30% shorter than that for both SBR formulations, compression sets greater than that for two of the controls but moduli significantly greater, and finally the permanent set and hardness indicated a different state of cure.

The original stress-strain and dynamic properties of the mercpto-telechelic copolymers were superior to those of the controls, and the dynamic properties of the aged stocks retained their position while the stress-strain properties were comparable.

Hydroxy-Telechelic Polymers Prepared in Solutions

Reactions of a lithium-telechelic polymer with reagents such as ethylene oxide, sym-trioxane, and oxygen under the proper conditions[18] result in the formation of hydroxy-telechelic polymers. The procedure of preparing a

low molecular weight polymer which possesses enough functional groups for analysis by a conventional method was used to estimate the telechelicity of these products.

The reaction of ethylene oxide with lithium-telechelic polybutadiene was affected by temperature. An example of this temperature effect on the hydroxyl content and telechelicity is shown by a typical experiment (Table VIII).

TABLE VIII
Effect of Temperature on Hydroxyl Content and Telechelicity[a,b]

Temp. for C_2H_4O reaction °C	hydroxyl %[c]	η_{inh}	Molecular weight based on			
			Initiator charged[d]	Hydroxyl analysis	η_{inh}[e]	tl^f
50	0.81	0.16	2770	5200	3600	0.66
121	0.98	0.12	2770	3470	2300	0.80

[a] Recipe: butadiene, 100 parts; cyclohexane 1560 parts; dilithiumstilbene initiator 40 mMHM: 50°C; 1.0 hr; 100% conversion.

[b] Reaction with ethylene oxide: lithium-telechelic polymer, 100 parts, ethylene oxide, 8.8 parts; 2.0 hr.

[c] Determined by the acetic anhydride–pyridine procedure.[19]

[d] Assumed all initiator and stoichiometric amount of ethylene oxide reacted.

[e] See Table V.

[f] Based on theoretical hydroxyl content of 1.23%.

The practical application of hydroxy-telechelic polymers will depend on the efficient utilization of the end groups in coupling or crosslinking reactions. Both dianhydrides and polyisocyanates are known coupling and crosslinking agents for hydroxy-telechelic polyethers and polyesters. Experiments with liquid hydroxy-telechelic polybutadiene and butadiene–styrene copolymers demonstrate the efficiency of coupling these polymers (Table IX).

The difunctional compounds, PMDA and TDI, reacted mainly as linear coupling agents since the coupled polymers showed no gel. However, with apolyfunctional agent, crosslinked products were obtained. For example a hydroxytelechelic polybutadiene with η_{inh} of 0.09 gave a product, after reacting with 7 phr of a polyaryl polyisocyanate (Papi-1 from Carwin Chemical Co.), that contained 61% gel, and of which the soluble portion had an η_{inh} of 0.34.

With the preceding results as guides, normal Mooney viscosity hydroxy-telechelic butadiene–styrene copolymers were prepared for evaluation. Cure studies showed that the enhancement of physical properties was obtained with the use of di- and polyisocyanates in peroxide cures of stocks containing 50 phr of Philblack O. Examples of some of the results obtained with different isocyanates and variable amounts of peroxides are given in Table X. Also included in this series of evaluations was a pair of stocks in which Dutrex 5 was used to give a lower modulus stock.

TABLE IX

Coupling Hydroxy-Telechelic Polymers with Pyromellitic Dianhydride (PMDA) or with Toluene-2,4-Diisocyanate (TDI)

Polymer	Li_2R, mMHM	Primary Molecular Weight data			Coupling Agent		Molecular weight after coupling[a]		
		η_{inh}	M_k	$\bar{M}_{kv}$	Type	mMHR	η_{inh}	$\bar{M}_{kv}$	n'
Hydroxy-telechelic butadiene–styrene copolymer	13	0.29	7970	9100	PMDA	15	1.17	79000	8.7[b]
Hydroxy-telechelic polybutadiene	40	0.11	2770	2000	TDI	2	0.15	3300	1.6
	40	0.11	2770	2000	TDI	3	0.27	8000	4.0
	40	0.11	2770	2000	TDI	4	0.42	15000	7.5[c]

[a] After 2–5 days at 71°C.
[b] Telechelicity is $U' = 0.89$.
[c] Telechelicity is $U' = 0.87$.

TABLE X

Hydroxy-Telechelic Butadiene Styrene Copolymer Cured with Peroxide and Di- or Polyisocyanate[a,b]

Di Cup 40 C, phr	Coupling agent		V_r	300% modulus, psi	Tensile, psi	Elongation, %	Resilience, %	ΔT, °F	Shore hardness
	Type[c]	Part							
1.0	—	—	0.406	—	2350	280	70	64	71
0.8	—	—	0.381	1050	2350	340	67	71	70
0.6	—	—	0.336	1100	1950	490	64	97	68
0.6	TDI	1	0.444	—	2750	260	77	45	75
0.6	N-5	1.2	0.450	—	2250	230	76	41	76
0.6	M	1.4	0.458	—	2450	220	77	37	75
0.6	Papi-l	1	0.461	—	2700	200	75	38	76
0.4	M	1	0.426	2250	3300	410	75	53	71
0.4	M	1.5	0.437	2600	3450	370	76	48	70
0.4	Papi-l	1	0.432	2700	3800	310	74	59	69
0.4	Papi-l	1.5	0.435	2750	3350	350	76	46	72
1.4[d]	—	—	0.393	1400	2150	430	68	90	69
0.55[d]	Papi-l	1	0.403	1550	3000	520	75	65	68

[a] Polymer 100 Philblack 0.50 parts; cure, 60 min at 153°C.
[b] 1.4 mMHM dilithiumorgano initiator used to prepare primary polymer that had a final ML-4 of 28 after hydroxylation.
[c] TDI, Tolylene-2,5-diisocyanate; N-5, naphthalene-1,5-diisocyanate; Papi-l, a polyisocyanate; M, p,p'-diphenylmethane diisocyanate (Mobay).
[d] Contains 5 phr Dutex; cured 30 min.

In general the use of the di- and polyisocyanates in the peroxide cure of the hydroxy-telechelic copolymers resulted in improvement of the stress-strain and dynamic properties as seen in Table X.

Another way of assessing the value of the di- and polyisocyanates in these peroxide formulations is to compare physical properties of stocks that have been cured to the same state as measured by V_r. In Table XI are data for three pairs of control and experimental stocks cured to approximately the same V_r.

TABLE XI
Hydroxy-Telechelic Copolymer Controls and Experimental
Stocks at Same State of Cure[a]

Di Cup 40 C, phr	Papi-1, phr	Cure time, min[b]	V_r	300% modulus, psi	Tensile, psi	Elongation, %	Resilience, %	ΔT, °F	Shore hardness
1.1	—	30	0.373	1300	2150	470	71	75	76
0.3	1	30	0.381	1570	2950	520	74	66	74
1.4	—	30	0.407	1900	2400	390	70	71	77
0.45	1	30	0.405	1800	2650	410	72	66	75
1.4	—	45	0.432	—	2310	280	70	68	78
0.55	1	30	0.423	2000	3250	450	74	52	75
0.55	1	45	0.445	2550	3250	360	76	51	76

[a] Ingredients common to the compounding formulation; copolymer, 100 parts; Philblack 0, 50 parts.
[b] Cure at 153°C.

The experimental stocks at approximately the same state of cure had superior stress-strain and dynamic properties. Although isocyanates are known to accelerate peroxide cures, the data for the experimental stocks show an enhancement that cannot be attributed simply to the rate of cure.

Aziridinyl-Telechelic Butadiene–Styrene Copolymers Prepared in Solution

Preparation of telechelic polymers possessing highly reactive groups can be readily accomplished by the methods used for the preceding polymers. As an example aziridinyl-telechelic butadiene–styrene copolymers were readily prepared by adding an excess of tris [1-(2-methyl)] aziridinyl phosphine oxide (MAPO) to a lithium-telechelic prepolymer.[20] These polymers could be easily isolated by coagulating in isopropyl alcohol.

The procedure used to determine telechelicity by measuring the viscosity of isolated polymers before and after coupling as in the preceding instances was not successful because of a marked tendency to form gel when difunctional coupling agents were used. Other evidence that a telechelic polymer was formed was the instantaneous formation of a jellylike solid after the functional terminating reagent was added to the polymerization solution. This behavior is characteristic of many telechelic polymers possessing ionic end groups.

Two low Mooney viscosity samples of aziridinyl-telechelic butadiene–

styrene copolymers were prepared by using two levels of dilithiumstilbene initiator and MAPO as the terminating agent (Table XII). These polymers were coagulated in isopropyl alcohol with the antioxidant present.

TABLE XII
Evaluation Samples of Aziridinyl-Telechelic
Butadiene–Styrene Copolymer[a,b]

	Viscosity	
Initiator, mMHM	η_{inh}	Mooney, ML–4
1.7	—	15
1.5	1.31	25

[a] Recipe: butadiene/styrene, 70/30 parts; cyclohexane, 780 parts; dilithiumstilbene initiator, variable; tetrahydrofuran, 1.5 parts; 50°C; 1 hr.

[b] Termination reaction: MAPO, 10 mMHM; 50°C; 1 hr.

A series of studies, conducted to find a satisfactory coupling agent for an aziridinyl-telechelic polymer, showed that polyacids coupled the polymer. Thiomalic acid, mercaptosuccinic acid, proved effective as a coupling agent in both sulfur and peroxide cure systems. The effect of variable amounts of thiomalic acid in a sulfur–accelerator cure of the 15 Mooney viscosity copolymer and SBR 1500 is shown in Table XIII.

Data in Table XIII show that thiomalic acid significantly improved the physical properties of the aziridinyl-telechelic polymer. The vulcanizate of the experimental telechelic polymer with 2.5 phr thiomalic acid had a tensile of 3900 psi, a heat build-up of 58°F, and a resilience of 77%. This is a better balance of properties than the control for the series and for controls such as those shown in Table VII. The thiomalic acid in SBR 1500 had adverse effects on these vulcanizate properties.

A tread evaluation of the 25 Mooney viscosity telechelic copolymer was conducted in which the experimental polymer was compounded with and without thiomalic acid. The control, SBR, was compounded at three accelerator levels to determine whether a tighter cure would result in physical properties comparable to those of the aziridinyl-telechelic elastomer (Table XIV).

The physical properties of the experimental polymer cured with thiomalic acid present are among the best for synthetic elastomers appearing in the literature. Noteworthy also are the properties of the aziridinyl control. The latter vulcanizate appears to be undercured since a notable improvement is seen for the 45 min heat build-up and the favorable balance of properties of the aged stock.

Another feature of the aziridinyl-telechelic polymers is the possibility of compounding this polymer with softeners possessing functional groups capable of reacting with the aziridinyl ends. Experiments with liquid carboxy-telechelic polybutadiene showed that these softeners were incorporated into the vulcanizate network and were not extracted after three days in ETA at 80°F.

TABLE XIII

Effect of Thiomalic Acid (TA) on Sulfur-Accelerator Cure of Aziridinyl Telechelic Copolymer and of SBR 1500[a,b]

	Aziridinyl-telechelic copolymer				SBR 1500			
	0 TA	1.0 phr TA	2.5 phr TA	5.0 phr TA	0 TA	1.0 phr TA	2.5 phr TA	5.0 phr TA
300% Modulus, psi	2600	2200	2500	2200	2000	1200	360	340
Tensile, psi	3200	3850	3900	3300	4050	3150	620	1200
Elongation, %	355	460	430	450	480	550	445	710
ΔT, °F	70	73	58	57	66	101	—[c]	—[c]
Resilience, %	74	75	77	78	63	56	50	51
Shore hardness	69	70	71	74	64	61	56	50

[a] Cure: 30 min at 153°C.
[b] Common ingredients: polymer, 100 parts; Philblack 0, 50 phr; ZnO/stearic acid, 3/1; Flexamine, 1.0 phr; sulfur/Santocure, 1.75/1.2.
[c] Too soft to run.

TABLE XIV
Tread Evaluation of an Aziridinyl-Telechelic
Copolymer and of SBR 1500 Control[a]

Properties	Aziridinyl copolymer		SBR 1500		
	1.0 phr Santo-cure	1.0 phr Santo-cure 2.5 phr TA	1.2 phr Santo-cure	1.4 phr Santo-cure	1.6 phr Santo-cure
Processing data					
Raw ML-4	25	25	54	54	54
Compounded, MS-1½	38	b	33	31	31
Scorch at 80°F, min	14	b	19	19	18
Extrusion at 450 F					
in/min	84	b	45	44	45
g/min	121	b	116	114	115
Rating	12–	b	12–	12	12–
Cure 30 min at 153°C					
V_r	0.384	0.414	0.392	0.402	0.407
Compression set, %	29	17	24	21	18
300% modulus, psi	1550	1600	1450	1600	1550
Tensile, psi	3500	4400	3600	4200	3800
Elongation, %	550	615	560	550	570
ΔT, °F	71	51	65	60	58
ΔT, °F (45 min)	55	43	63	60	58
Resilience, %	73	75	60	61	62
Shore hardness	63	65	60	61	62
Oven-aged 24 hr at 100°C					
300% modulus, psi	2100	2400	2300	2400	2250
Tensile, psi	3800	4000	3350	3300	3400
Elongation, %	480	480	410	450	420
ΔT, °F	47	41	54	51	51
Resilience, %	77	77	67	69	68

[a] Common ingredients: polymer, 100 parts; Philblack 0, 50 phr; ZnO/stearic acid, 3/1; Flexamine 1 phr; Philrich 5, 10 phr.
[b] Not determined.

The vulcanizate data for the aziridinyl-telechelic polymers show that a considerable latitude exists for the compounder working with telechelic polymers possessing very reactive end groups.

DISCUSSION

The successful application of telechelic elastomers depends first on the attainment of a high telechelicity and then on an efficient coupling or an incorporation of telechelic polymers from hydrocarbon monomers, as distinguished from heteromonomers or condensation polymerization which inherently produce terminal functional groups, has presented some problems in the past. If a polymerization system based on a free-radical mechanism is used, one is forced to employ an initiator or a transfer agent that possesses

the desired functional group.   No one class of free radical initiators exists or can be readily converted into compounds possessing a variety of functional groups; although specific initiators, such as azobisalkylcarboxylates[21,22] or diazothioethers[1] have been used successfully.   Bis-type transfer agents have been intensively examined for the preparation of telechelic polymers[7,8] but again only a limited number have been used successfully.[23]

For the preparation of telechelic polymers, the anionic polymerization systems are quite versatile.   Dialkalimetalloorganic compounds readily polymerize reactive olefin monomers to metallo-telechelic polymers.   The chemistry and reactivity of these terminal groups is essentially the same as that for the small molecules and accordingly the potential for synthesis of telechelic polymers is just as great.   For the preparation of elastomers from diene monomers, the dilithioorganic compounds are preferred because of the higher telechelicity obtainable.   The polymers reported here represent only a few of those that were usable in sulfur vulcanization formulations.

Mercapto-Telechelic Polymers Prepared in Latex

Dixie is a fairly efficient modifier in emulsion polymerization of butadiene-styrene mixtures.   A comparison can be made with tert-dodecyl mercaptan used for the control polymer, Table II, and by a comparison of the modification parameters for both modifiers.[24]   Molecular weight measurements of diene polymers prepared with radioactive xanthate modifier indicated that possibly more than two xanthate groups are present per polymer molecule.[25] The molecular weights of the polymer calculated by two methods agree reasonably well in view of the assumptions made for the calculations (Table II).

Hydrolysis of the xanthate-telechelic polymer with hydrazine as a catalyst in hydrocarbon solutions leads to near quantitative conversion of the xanthate to mercaptan.   By following the mercapto content quantitatively, one can likewise obtain high conversion of xanthate to mercaptan in emulsion systems (Fig. 1).

Besides the analytical evidence of mercapto groups attached to the polymer, the high rates of cure and the tendency to scorch in standard vulcanization systems signal the presence of a highly reactive polymer.   The curing of GRS with dithiol is worth noting in this connection.[26]   Despite the low level of accelerator used and the low state of cure for the mercapto-telechelic polymer (Table IV) a reasonable balance of properties was reached which improved under aging conditions.   Mercapto-telechelic polymers will be discussed further in a following section on solution polymerization.

Coupling Lithio-Telechelic Polymers

The number of agents capable of coupling these telechelic polymers is almost as great as the number of functional groups that react with organometal compounds.   For the purpose of determining coupling efficiency by the viscosity procedure, the agent needed is one that gives a linear coupled

TABLE XV
Telechelicity Required for a Series of Primary Telechelic
Polymers to Give a Coupled Polymer of 150,000 MW

Primary molecular weight	Coupling required, n	$tl = (n - 1)/n$[a]
500	300	0.9967
1000	150	0.9934
5000	30	0.967
10000	15	0.934

[a] Fraction of chain ends possessing a functional group.

polymer. Of the various agents tested for producing a linear coupled polymer, the bis(chloromethyl) ether was found to be one of the most effective.[27]

The method of calculating telechelicity tl is similar to that proposed by others.[28] The need of a high telechelicity is seen from a calculation to determine the coupling required for a series of primary molecules to give a final molecular weight of 150,000 (Table XV).

The data in Table XV show the difficulty a chemist may encounter in preparing a liquid telechelic polymer for elastomeric applications. If an excess of initiator is used to swamp the impurities in the polymerization system, then side reactions during polymerization, such as chain transfer, transmetallation, and hydride formation, could become troublesome. On the other hand, if less initiator is used, slow reacting impurities as well as side reactions may become troublesome.

An exact relationship can be obtained from intrinsic viscosities for coupled and uncoupled semitelechelic polymers if the primary polymer is monodispersed. If the number-average degree of coupling is $n = (\bar{M}_n$ coupled$)/(M_n$ primary$)$ and $B = [\eta_{coupled}]/[\eta_{primary}]$ and $[\eta] \doteq K\bar{M}_n{}^a$; then $n = (2 - 2^{1+a})/(B + 1 - 2^{1+a})$. The actual use of inherent viscosity in place of intrinsic viscosity introduces only a small error, since the correction tends to cancel out in calculating B. The values in Table V for the semitelechelic-lithio polymers are probably minimum measures of the degree of coupling; since they represent both dead polymers and efficient coupling. The high efficiency of coupling organometal compounds with active halogen reagents is recognized in the use of a coupling reaction in Gilman's double titration procedure for analyzing organometal compounds.

Greater uncertainties are introduced into the determination of coupling efficiencies when viscosity average molecular weight is used as in the case of lithium-telechelic polybutadiene recorded in Table V. The primed values are used to indicate apparent degree of coupling and telechelicity. However, the 9-fold increase in inherent viscosity in one instance is noteworthy; and if the polymers were monodispersed and the viscosities were intrinsic, the calculated molecular weight would represent a degree of coupling of approximately 26. Coupling factors as high as these have been reported in the literature for sodio-telechelic polystyrene.[28] The experimental data

show the lithio-telechelic prepolymers should be excellent precursors for preparing other telechelic polymers.

Mercapto-Telechelic Butadiene–Styrene Copolymers Prepared in Solution

The preparation of small mercaptan molecules by the addition of sulfur to organometal compounds is complicated by side reactions.[29]   In the preparation of mercapto-telechelic polymers, mercapto contents as high as those given in the literature for small molecules were attained in some experiments.   Some of these polymers were quite reactive and tended to scorch during processing.   For this evaluation a polymer with a lower mercapto content was prepared.

The mercapto polymer prepared in solution was easier to compound than was the polymer prepared in an emulsion system.   The lack of scorch was attributed to the lower mercapto content of the polymer.   Although the compression set shows a lower state of cure for the experimental polymers than for the laboratory control, the stress-strain and dynamic properties are characteristic of a high state of cure (Table VII).   This combination of properties can be attributed to a more efficient participation of the polymer molecules in the vulcanizate.

Hydroxy-Telechelic Polymers

The preparation of an alcohol by addition of the epoxide to an organometal compound is well known.   For the preparation of hydroxy-telechelic polymers a high hydroxyl content was obtained by conducting the reaction in cyclohexane and heating the solution for a relatively long time after the addition of the ethylene oxide.   The molecular weight of the polymer was readily controlled by the amount of initiator, and the reaction with ethylene oxide introduced no apparent side reaction.   The telechelicity, as judged by chemical analyses and coupling reactions, was high (Tables VIII and IX).

The combination of diisocyanates and peroxides function as an effective cure system.   The use of diisocyanates in polyurethane cures is well known and the chemistry of these systems is adequately reviewed in current literature.[30,31]   The improvement of the experimental polymers in comparison to the controls is attributed to a coupling of the chains with the diisocyanate and a crosslinking of the polydiene portion by free radicals from the peroxide.   Of course, crosslinks could also arise from side reactions of the isocyanate groups and the coupled linkages.   A comparison of the control and experimental polymers at equal states of cure (Table XI) show again a better balance of properties for the experimental stocks which give higher stress-strain and better dynamic properties.

Aziridinyl-Telechelic Polymers

These polymers, although difficult to characterize, proved the most interesting in sulfur vulcanization studies.   The chemistry of carboxylic acids and aziridinyl compounds is being reported in current literature[32] and need not be presented here.

The marked difference the thiomalic acid has in the aziridinyl and the SBR control polymer is shown by the data in Table XIII. As established for the curing of carboxyl-telechelic polybutadienes with MAPO,[33] thiomalic acid undoubtedly couples aziridinyl-telechelic polymer. The incorporation of liquid carboxy-telechelic polybutadiene in the aziridinyl polymer vulcanizate also supports this reaction. The thiol group can participate in crosslinking reactions as has been found for other polymers possessing mercapto groups. A similar sequence of reactions was predicted for the vulcanization of acetyltelechelic polymers with the aid of mercaptostearylhydrazide.[1]

The aziridinyl polymer in a tread formulation with thiomalic acid exhibited an exceptional balance of properties for a synthetic rubber (Table XIV). Even though the cure was not much tighter (as judged by V_r, compression set, and modulus), the tensile, elongation, heat build-up, and resilience were superior to those of any of the controls.

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