

Anionic telomerization of butadiene with toluene and diphenylmethane: microstructure and molecular weight

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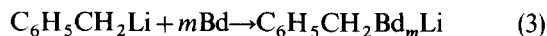
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The frequency of chain transfer of polybutadienyllithium to toluene and diphenylmethane is increased in the presence of *N, N, N', N'*-tetramethylethylenediamine. When the reactor is fed with monomer at a constant rate, the molecular weight of telomer falls steeply as the ratio [base]:[lithium] increases from zero to unity but much more slowly thereafter. Whenever an anionic chain end has a penultimate 1,2-placement, cyclization to form a vinylcyclopentane competes with propagation the more favourably the lower the monomer concentration. In consequence, telomers prepared in toluene have a far greater cyclic content than those prepared in diphenylmethane.

(Keywords: butadiene, *N, N, N', N'*-tetramethylethylenediamine; telomerization; anionic polymerization; polybutadienyllithium)

INTRODUCTION

Organolithium compounds are particularly attractive initiators of the polymerization of conjugated dienes since the stereochemical course of the propagation reaction can be controlled to a considerable extent by suitable choice of solvent. In hydrocarbon solvents 1,4-enchainment predominates whereas in solvating media such as tetrahydrofuran (THF) the 1,2- or 3,4- structures are generally favoured; intermediate behaviour is observed when small quantities of Lewis bases are added to the hydrocarbon media. Conditions can often be found under which there is neither transfer nor termination, thereby permitting the synthesis of materials of predictable molecular weight and of low dispersity. However, when polymers having very low molecular weights are sought, the high cost of lithium becomes a serious economic consideration. Provided that a product of rather broad molecular weight distribution is acceptable, a simple solution is to operate under conditions favouring chain transfer. By way of illustration, if butadiene (Bd) is polymerized by an organolithium initiator (RLi) in the presence of toluene, proton transfer from the methyl group terminates the chain growth forming benzyl lithium which is a very rapid initiator of butadiene polymerization:



In consequence, every lithium atom is potentially capable of generating many polymer molecules. However, under conventional conditions of concentration and tempera-

ture, the frequency of chain transfer with toluene is unacceptably low unless a promoter such as *N, N, N', N'*-tetramethylethylenediamine (TMEDA) is present^{1,2}. In addition to enhancing transfer, TMEDA additionally engenders a cyclization reaction³ involving those anionic ends having a penultimate 1,2-placement:



The results of a preliminary comparison of the propensities of TMEDA and THF to cause cyclization have been published⁴: it was found that the cyclic content of the resulting polymers was much higher when formed in the presence of TMEDA than in that of THF. The present work was undertaken to investigate the influence of the base: lithium ratio and the effect of employing a stronger acid (viz. diphenylmethane) as chain transfer agent upon the micro-structure and molecular weight of polybutadiene.

EXPERIMENTAL

Cyclohexane and toluene were allowed to stand over finely ground calcium hydride for several days, decanted into and distilled from butyllithium and stored over Linde 4A molecular sieves under nitrogen.

Diphenylmethane was fractionated under vacuum. TMEDA was distilled under nitrogen from calcium hydride and stored over Linde 4A molecular sieves.

Telomerization was conducted in a 2 l glass reactor fitted with a stirrer and an alcohol-solid CO₂ condenser. A 2.5 molar solution of telogen (total volumes 600 or 654 cm³ respectively when toluene or diphenylmethane was employed) containing the appropriate quantity of

Table 1 Dependence of stationary state monomer concentration (mol l^{-1}) upon promoter and polymer content

[TMEDA]:[Li]	Approximate polymer content (wt%)		
	18	35	50
Toluene as telogen			
0.10	0.11		
0.25	0.047	0.037	0.033
0.50	0.052		
0.75	0.034		
1.00	0.039	0.034	0.030
2.5	0.049		
5.0	0.045	0.052	0.031
Diphenylmethane as telogen			
0.10	0.079	0.077	
0.25	0.063	0.069	0.031
0.50	0.058	0.061	
0.75	0.066	0.035	0.057
1.00	0.10		
2.5	0.25	0.15	0.093

TMEDA was introduced together with $\sim 0.5 \text{ cm}^3$ styrene. The reactor was flushed with nitrogen and n-butyllithium solution was added slowly and dropwise until a faint permanent colouration due to styryl-lithium persisted, indicating complete freedom from oxygen and protogenic impurities. Sufficient n-butyllithium was then added to make the reaction mixture 0.063 molar in this substance and the temperature was raised to 75°C . Butadiene was passed through a column of Linde 3A molecular sieves to remove moisture and was metered into the reactor at a constant rate of 1 l min^{-1} through a calibrated rotameter. The reactor temperature was maintained at $75 \pm 1^\circ\text{C}$ and aliquots of the reaction mixture were withdrawn at intervals, terminated with glacial acetic acid and analysed for residual monomer by g.l.c. Polymer molecular weights were determined by g.p.c. using a Waters instrument having a six column styragel set with porosities ranging from 10^2 to 10^6 \AA . Polymer microstructures were determined using a 220 MHz n.m.r. spectrometer (Perkin Elmer R34) and the polybutadiene assignments provided by Tanaka *et al.*⁵.

RESULTS AND DISCUSSION

In order to study the influence of the base:lithium ratio upon the properties of the resulting polymers, the temperature and the starting concentrations of the initiator and the telogen were held constant. Although the flow rate of the butadiene into the reactor was also held constant, and escape of unconsumed monomer was negligible, it cannot be assumed that the concentration of monomer in the reaction mixture was necessarily also invariant unless the same stationary state concentrations of allylic and aryl methyl anions were always established quickly. Furthermore, with the lapse of time, the contents of the reactor became somewhat diluted by the accumulation of polymer; in practice, the maximum (final) dilution was ca. $\times 1.6$. To assess the variation in monomer concentration during the progress of the polymerization, aliquots were withdrawn from the reaction mixture and analysed by g.l.c. when the accumulated polymer amounted to ca. 18, 35 and 50% by weight. The results (*Table 1*) show that with toluene as telogen, the monomer concentration was sensibly constant for $[\text{base}]:[\text{lithium}] \geq 0.1$ with, perhaps, a slight tendency to decrease as the polymer content

increased. The concentration of monomer was distinctly higher when diphenylmethane was employed as the telogen—especially when the base:lithium ratio was equal to, or greater than, unity. The microstructures of the polymers formed in the presence of these two telogens are summarized in *Table 2*. Increasing the content of TMEDA resulted in a decreasing proportion of enchainment in a 1,4-sense; ^1H n.m.r. spectroscopy has shown⁶ that complexation of polybutadienyllithium causes an increase in charge density at the anionic γ -carbon atom. With both telogens, significant proportions of cyclic structure were formed when the base:lithium ratio was ≥ 0.25 : what is particularly interesting is that the cyclic content was so very much greater with toluene than with diphenylmethane under comparable conditions. Since diphenylmethane is a stronger acid than toluene (pK values are ca. 33 and 41 respectively) it would be anticipated to participate more readily in transferring a proton to polybutadienyllithium. Since the diphenylmethyl anion is a weaker base than benzyl anion it would be expected to be a less active initiator. Consequently, the stationary state concentration of growing chains should be smaller, and that of monomer greater, in the presence of diphenylmethane: *Table 1* verifies the latter conclusion. Since cyclization has to compete with propagation, it is favoured by lower concentrations of monomer and, accordingly, the cyclic content of the polymer formed in the presence of toluene is greater. As previously noted, complexation of the anionic chain end with base is a prerequisite for cyclization¹.

The formation of a vinylcyclopentane residue in polybutadiene requires a transition state in which the propagating centre has a penultimate 1,2-placement. If ring

Table 2 Dependence of polymer microstructure upon promoter level and telogen

Run	[TMEDA]:[Li]	Microstructure*		
		1,4	1,2	Cyclic
Toluene as telogen				
R13	0.10	62	38	--
R6	0.25	51	37	12
R12	0.50	32	30	38
R10	0.75	27	20	52
R7	1.00	23	17	60
R11	2.5	26	13	61
R8	5.0	23	17	60
Diphenylmethane as telogen				
R19	0.10	69	31	--
R14	0.25	50	34	16
R16	0.50	40	36	24
R17	0.75	33	34	33
R9	1.00	33	43	24
R18	2.5	36	47	17
R15	5.0	35	46	19

* Proportions expressed in wt%

Table 3 Percentage 1,2-content calculated on an equivalent basis*

Telogen	[TMEDA]:[Li]						
	0.10	0.25	0.50	0.75	1.00	2.5	5.0
Toluene	38	45	58	58	60	54	60
Diphenylmethane	31	45	54	59	62	60	61

* The equivalent basis is defined in the text; the balance of the equivalent structure is 1,4-

Table 4 Dependence of polymer molecular weight (kg mol^{-1}) upon promoter concentration

Run	TMEDA Li	1,4-calc.*		1,2-calc.†		Weighted‡		Dispersity
		\bar{M}_n	\bar{M}_w	\bar{M}_n	\bar{M}_w	\bar{M}_n	\bar{M}_w	
Toluene as telogen								
R13	0.10	16.0	17.7	19.2	21.3	17.1	19.1	1.12
R6	0.25	11.7	13.9	14.1	16.8	12.9	15.3	1.19
R12	0.50	4.9	9.9	6.0	12.0	5.7	11.3	1.98
R10	0.75	2.0	5.3	2.4	6.4	2.3	6.1	2.65
R7	1.00	1.5	3.9	1.9	4.7	1.8	4.5	2.50
R11	2.5	1.0	2.4	1.2	2.9	1.2	2.8	2.33
Diphenylmethane as telogen								
R19	0.10	12.8	15.4	15.4	18.5	13.6	16.3	1.20
R14	0.25	3.2	7.5	4.0	9.1	3.6	8.3	2.30
R6	0.50	1.4	3.5	1.8	4.2	1.6	3.9	2.44
R17	0.75	0.93	2.2	1.1	2.7	1.1	2.5	2.27
R9	1.00	0.93	2.1	1.1	2.6	1.1	2.5	2.27
R18	2.5	0.37	0.73	0.45	0.90	0.42	0.84	2.0
R15	5.0	0.33	0.82	0.40	1.0	0.37	0.94	2.54

* Calculated from g.p.c. elution peak assuming all 1,4-microstructure

† Calculated from g.p.c. elution peak assuming all 1,2-microstructure

‡ Calculated from (a) and (b) by weighting these on the basis of actual microstructure

closure did not occur, the carbanion would be converted into either an in-chain 1,2- or 1,4-placement with the same relative probabilities as the placements that constitute the non-cyclic portion of polybutadiene. Subdividing one half of the cyclic content into its equivalent potential 1,2- and 1,4-enchainment, and treating the other half of the cyclic content as latent 1,2-structure enables one to describe the overall observed structure of the polymer in terms of the equivalent propagation in a 1,2 or 1,4-sense, that is in terms of a single variable. Table 3 presents the results of analysis of the data in terms of 1,2-addition. Clearly, the equivalent mode of addition is independent of the nature of the telogen. This fact is not obvious from Table 2. It is apparent that the 1,2-content increases with increasing proportions of TMEDA and that a ceiling value of about 60% is reached when the TMEDA:lithium ratio is equal to or greater than 0.75. Presumably, a single species (most probably the non-aggregated chain end complexed with a single molecule of TMEDA) then dominates the propagation process.

The interpretation of g.p.c. data to determine the molecular weight and the molecular weight distribution of the polymers is complicated by the varying stereochemistry. In an attempt to reduce, albeit not completely remove, the influence of this factor the following procedure was employed. As shown in Table 4, the \bar{M}_n and \bar{M}_w values were calculated from the g.p.c. traces assuming successively that the polymers were all 1,2- and all 1,4-enchainment. The resulting values were then combined, weighted in proportion to the weight fraction of these structures established from the ^1H n.m.r. spectra; for the purposes of computation, the cyclic content was combined with the 1,2-content.

The data of Table 4 show that as r increases the molecular weight of the polymer decreases, in accordance with the known ability of TMEDA to stimulate chain transfer. The influence upon molecular weight is very dramatic for values of r less than unity; larger values of r cause only a modest further decrease. These observations could be accounted for by the formation first of a 1:1 complex between polybutadienyllithium and TMEDA having high reactivity towards transfer, followed by the formation of some complex containing more TMEDA and of only slightly greater reactivity. Support for this

proposal is provided by ^1H n.m.r. spectroscopy⁶ and by concentrated solution viscometry⁷. Table 4 further shows that, for any given value of r , the molecular weight of the polymer produced in the presence of diphenylmethane is always smaller than when toluene is used: this is as expected on the basis of the greater acidity of the former solvent. A parallel observation is that the dispersity of the molecular weight distribution is increased more with diphenylmethane than with toluene for $r \leq 0.5$.

An unexpected property of the polymers prepared in the presence of diphenylmethane was that they exhibited a blue fluorescence; no such fluorescence could be detected in the polymers prepared in toluene. The excitation (λ_{max} 360, 379 and 398 nm) and the emission spectra (λ_{max} 408, 429 and 454 nm) very closely resembled those of anthracene. The fluorescence was not removed by repetitive precipitation of the polymer into methanol and it was concluded that the chromophore was covalently bound to the polymer. Assuming that an anthracene moiety was indeed present, an estimate can be made of the concentration by taking the molar extinction coefficient at 398 nm as $10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$. On this basis, the concentration fell smoothly from 9.4×10^{-2} to 2×10^{-3} mol per cent as r increased from 0.1 to 1.0. These low levels show that the process leading to the formation of the polycyclic aromatic is of minor importance kinetically; it is, however, likely that the photochemical stability of these polybutadienes will be affected.

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