Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Dynamic Mechanical Properties of Some Polycaprolactone-Based, Cross-Linked, Crystallizable Polyurethanes

W. K. Busfield[a]
[a] School of Science Griffith University, Nathan, Queensland, Australia

To cite this Article Busfield, W. K.(1982) 'Dynamic Mechanical Properties of Some Polycaprolactone-Based, Cross-Linked, Crystallizable Polyurethanes', Journal of Macromolecular Science, Part A, 17: 2, 297 — 309
To link to this Article: DOI: 10.1080/00222338208063262
URL: http://dx.doi.org/10.1080/00222338208063262

J. MACROMOL. SCI.–CHEM., A17(2), pp. 297-309 (1982)

Dynamic Mechanical Properties of Some Polycaprolactone-Based, Cross-Linked, Crystallizable Polyurethanes

W. K. BUSFIELD

School of Science
Griffith University
Nathan, Queensland 4111, Australia

ABSTRACT

The dynamic mechanical properties of some cross-linked and crystallizable polyurethanes based on polycaprolactone have been investigated with a Rheovibron Elastometer in the temperature range 150-370 K. Crystallizable samples have been studied in both quenched and annealed forms. Cold crystallization of the quenched forms occurs a few degrees above the glass temperature. Structural factors influencing both ease of crystallization and decrease in glass transition temperature are (a) decrease in cross-link density, (b) increase in MW of polycaprolactone segment, and (c) use of a flexible aliphatic diisocyanate as linking agent rather than aromatic types.

INTRODUCTION

This paper describes the dynamic mechanical properties of a series of polycaprolactone based, lightly cross-linked polyurethanes, made by the one-shot method. The polymers were made and tested by Guise and Smith [1] with the aim of producing a soft, durable rubber for a certain practical application. Some of the samples were found to crystallize to tough elastomers under certain conditions and, although this rendered them unsuitable for practical application, it became of interest from the academic viewpoint to make a closer study of the factors which influence crystallization in the somewhat unusual environment of a cross-linked matrix. This is the first report on the dynamic mechanical properties of these polymers. Previous work on polycaprolactone-based polyurethanes has been on linear polymers, usually containing low molecular weight chain extenders, or on polymers made by the two-shot (prepolymer) method [2-5].

EXPERIMENTAL

Polymers

Details of the methods of preparation and casting the polymers have already been described [1]. Briefly they were made by a one-shot method from a mixture of a caprolactone oligomeric diol, a caprolactone oligomeric triol, and a diisocyanate. All had stoichiometric equivalence of hydroxy and isocyanate groups. The composition of samples used in this work are given in Table 1. They were chosen with the objective of studying the effects of (a) cross-link density (Samples 29, 31, and 33), (b) diol molecular weight (Samples 1, 17, and 31), and (c) the nature of the isocyanate (Samples 17, 20, and 21).

Rheovibron

Test samples, cut directly from the castings, had dimensions in the range 8-11 mm long and 2-4 mm^2 cross-section. Initial tests were done on samples as received, i.e., after several months storage at ambient temperature. After cooling the samples in the instrument with a stream of precooled nitrogen gas to about 150 K over a period of 12-20 min, the mechanical loss tangent (tan δ) and the complex modules (E^*) for a sinusoidal tensile strain at a fixed frequency were measured "on the run" at temperature intervals of 2-5°, depending on the region of interest, as the sample was heated at 2-3°/min to about 370 K. E^* was calculated on the assumption that the sample cross-section was temperature independent.

Following the first run, samples which were initially partially crystalline (21, 33, and 31) were heated to 420 K under slight tension and quenched in liquid nitrogen while still mounted in the instrument. A second series of measurements of tan δ and E^* were taken for the quenched sample in the same temperature range as the first. Results of these experiments are labeled with the suffix Q.

Melting temperatures of semicrystalline samples were taken as the intersecting point of the extrapolated descent of the log E^*/T curve

TABLE 1. Composition Data

Sample no.	Isocyanate[a]	Diol MW	Triol MW	Mass content (%) Diol	Triol	Iso	Chain atoms[b] per cross-link
1	TDI	530	540	59	15	26	187
17	TDI	2000	540	68	17	15	169
20	MDI	2000	540	64	16	22	183
21	HDI	2000	540	68	17	15	177
29	TDI	3000	540	55	28	17	102
31	TDI	3000	540	71	18	11	167
33	TDI	3000	900	89	5	7	1086

[a] TDI, tolylene diisocyanate; MDI, methylene bis(4-phenyl isocyanate); HDI, 1,6-hexane diisocyanate.

[b] Calculated from the molar ratios of reactants assuming 1 triol molecule produces 1 cross-link.

with the extrapolated rubbery plateau. Most experiments were performed at 11 and 110 Hz. For Sample 1, experiments were also performed at 3.5 and 35 Hz.

Differential Scanning Calorimetry (DSC)

Glass temperatures were determined for each sample by DSC (Perkin-Elmer Model 2). Prior to each run, the sample was cooled as rapidly as possible in the instrument from above the melt temperature to below T_g in order to ensure the absence of crystalline material. The heating rate was 20 K/min and the temperature scale was calibrated by the melting point of mercury. Glass temperatures were taken as the intersecting point of the extrapolated pretransition baseline and the line passing through the inflection.

Dielectric Constant

The temperature of maximum dielectric loss for Sample 1 at a frequency of 1590 Hz was measured with a Wayne Kerr Bridge. The sample was a cylindrical section length 3 mm, cross-section diameter 60 mm, wedged between stainless steel electrodes. Measurements of tan δ_ϵ were made at intervals of 1 K as the sample temperature was raised from 280 to 315 K over a period of 3 h.

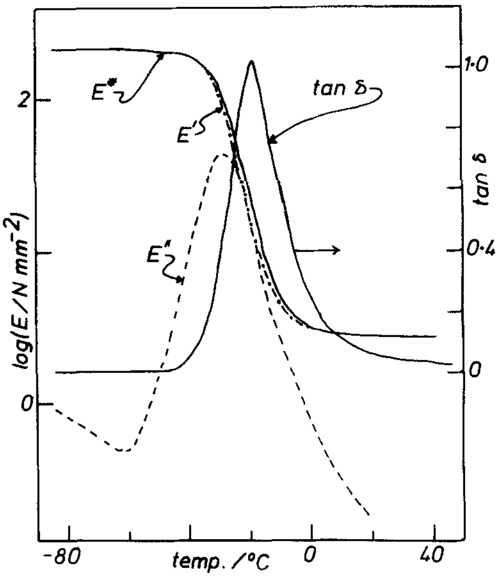

FIG. 1. The relation between the dynamic complex modulus (E*), dynamic storage modulus (E'), dynamic loss modulus (E"), and dynamic loss tangent (tan δ) as a function of temperature for Sample 17.

TABLE 2. Different Measures of the Glass Transition Temperature

	$(T_{max})_\delta$ (°K)		$(T_{max})_{E''}$ (°K)		$(E_a)_\delta{}^a$	T_g (°K)
Polymer	11 Hz	110 Hz	11 Hz	110 Hz	(kJ/mol)	(DSC)
1	284	294	278	286	168^a	260
17	254	261	245	249	169	223
20	259	267	252	257	166	232
21Q	235	239^b	228	235	269	216
29	261	270	249	256	159	223
31Q	249	255^b	240	240^b	221	221
33Q	230	^{c}	225	226^b	-	214

[a] Energy of activation calculated from $(T_{max})_\delta$ values at 11 and 110 Hz. For Sample 1, $(E_{act})_\delta$ calculated over the full frequency range of measurements (Fig. 2) is 215 kJ/mol.

[b] May be inaccurate due to the close incidence of cold crystallization.

[c] Obscured by cold crystallization.

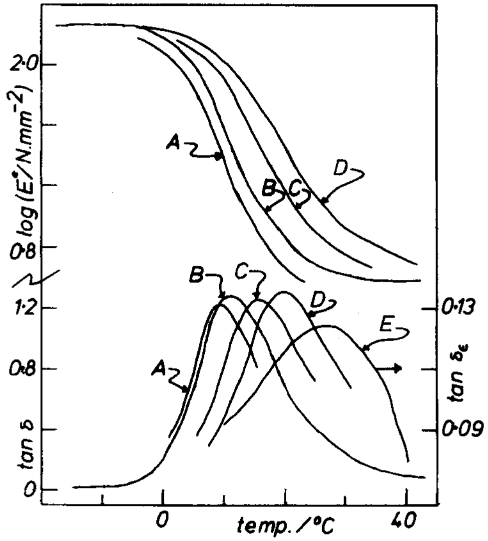

FIG. 2. The effect of frequency on the dynamic complex modulus and the dynamic loss tangent/temperature curves for Sample 1. A, 3.5 Hz; B, 11 Hz; C, 35 Hz; D, 110 Hz; and E, dielectric loss tangent ($\tan \delta_E$) at 1590 Hz.

RESULTS

The interrelationships between log E^* (complex modulus) and log E' (real component of E^*) and between $\tan \delta$ (mechanical loss tangent) and log E'' (imaginary component of E^*) are illustrated as a function of T for a typical noncrystallizable sample (Sample 17) in Fig. 1. Graphs of both $\tan \delta$ and log E'' exhibit single peaks associated with the glass transition, with peak maxima given in Table 2 as $(T_{max})_\delta$ and $(T_{max})_{E''}$, respectively, for measurements made at both 11 and 110 Hz. The magnitude of the difference $[(T_{max})_\delta - (T_{max})_{E''}]$ is greatest for the most heavily cross-linked sample (Sample 29) and least for the sample with lightest cross-linking (Sample 33Q), in keeping with the knowledge that peaks generally become broader with cross-linking. The result of varying the frequency of stress application, f, for a typical noncrystallizable sample (Sample 1) is shown in Fig. 2. The frequency range was extended by measuring the dielectric loss tangent as a function of temperature at 1590 Hz. The effect of f on T_g is related to the energy of activation, E_a, associated with the onset of the molecular motion which gives rise to the transition, by the Arrhenius relation [6]:

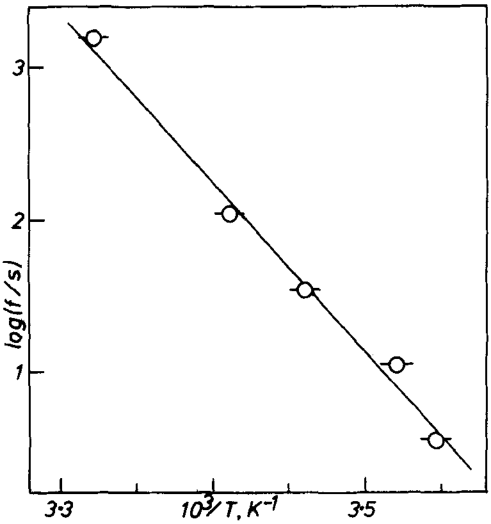

FIG. 3. Graph of log frequency against $(T_{max})_{\delta}^{-1}$ for Sample 1.

$$\ln f = -(E_a/RT_g) + \text{const}$$

A graph of log f vs $(T_{max})_{\delta}^{-1}$ for Sample 1 gives a reasonable linear plot, Fig. 3, resulting in an activation energy of 215 kJ/mol. Activation energies for other samples, given in Table 2, have been calculated from measurements on the Rheovibron at two frequencies only (11 and 110 Hz). Note that for Samples 21Q and 31Q, $(T_{max})_{\delta}$ may be low due to the onset of cold crystallization (see later); this would result in a high value of E_a for these samples. The precision in E_a is about ± 50 kJ/mol [based on a precision of ± 1 K in the $(T_{max})_{\delta}$ values]. Glass temperatures measured by DSC are also included in Table 2 for comparison with $(T_{max})_{\delta}$ and $(T_{max})_{E''}$ values. As expected from the essentially static nature of the experiment, $(T_g)_{DSC}$ values are lower by 16 to 38 K than the corresponding $(T_{max})_{\delta}$ values. The lower and higher difference values refer to the most lightly and most heavily cross-linked samples, respectively, suggesting qualitatively that E_a decreases with increased cross-linking in comparison with the values of E_a listed in Table 2.

The results of the dynamic mechanical experiments on the Rheovibron for polymers of various cross-link densities, segment lengths, and linking units are illustrated in Figs. 4, 5, and 6, respectively.

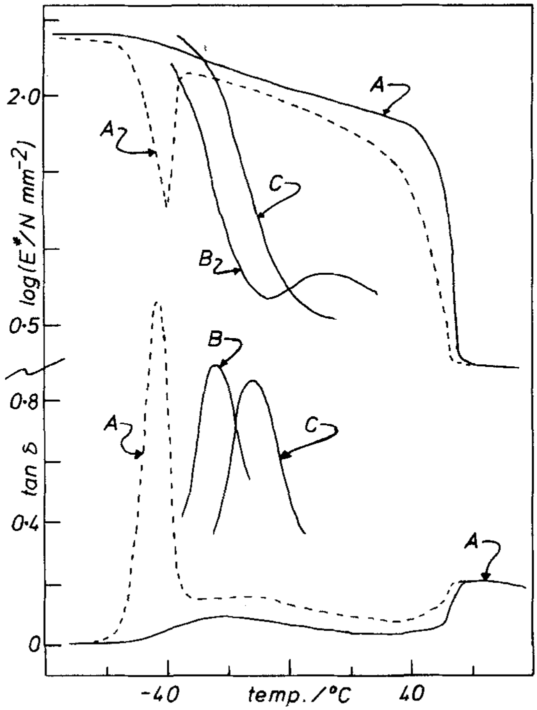

FIG. 4. Dynamic complex modulus and dynamic loss tangent curves as a function of temperature for samples of varying cross-link density. A, Samples 33 annealed (full lines) and 33Q, quenched (broken lines); B, Sample 31Q; and C, Sample 29. Only the transition regions of B and C are shown for clarity.

The complex modulus curves for Samples 21, 31, and 33 in their annealed state are typical of those of semicrystalline polymers in general except in the higher temperature range, where E* levels off at a value typical of a rubbery plateau. This is due to the presence of cross-links which are not normally present in semicrystalline polymers. All other samples exhibit E* and tan δ curves typical of lightly cross-linked, amorphous polymers. As was deduced from earlier tests [1], these results indicate that crystallization in these series of polymers is facilitated by (a) decreasing cross-link density, (b) increasing length of polycaprolactone segment, and (c) using a flexible aliphatic diisocyanate as linking unit.

Crystallization is easily prevented in Samples 21, 31, and 33 by quenching with liquid nitrogen from the melt. The dynamic mechanical properties of the quenched forms are shown as a function of

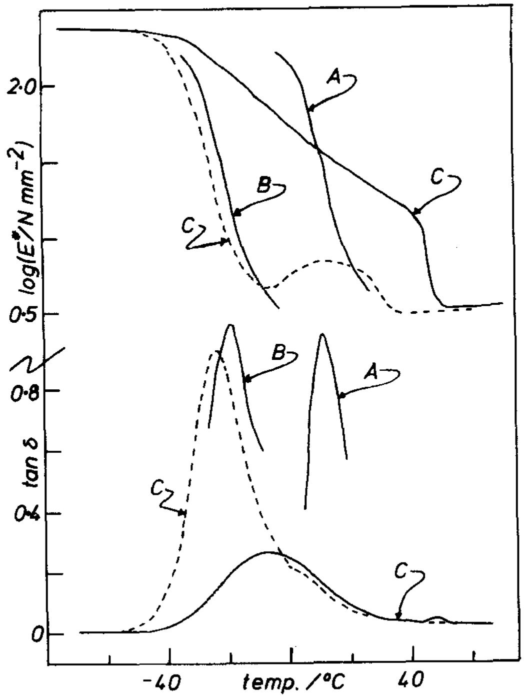

FIG. 5. Dynamic complex modulus and dynamic loss tangent curves as a function of temperature for samples of varying segment length. A, Sample 1; B, Sample 17; and C, Samples 31 annealed (full lines) and 31Q, quenched (broken lines). Only the transition regions of A and B are shown for clarity.

temperature by the dotted curves in Figs. 4 to 6. The samples behave like typical amorphous polymers up to a few degrees above the onset of the glass to rubber transition, as denoted by the position of the mechanical loss peak. A sharp increase in E* then indicates the commencement of cold crystallization at 233 and 239 K for Samples 33Q and 21Q, respectively, while cold crystallization occurs much more sluggishly in Sample 31Q starting at 268 K, 19 K above $(T_{max})_\delta$. In all three samples, cold crystallization produces less perfect crystallites than are present in the corresponding annealed forms, as illustrated by the less steep approach of the log E*/T curve to the melting point, T_m, and the lower value of T_m (see Table 3). This feature is presumably due to the higher nucleation rate which occurs at lower temperatures. Further evidence for this is given by the following two observations: (1) crystallization at room temperature

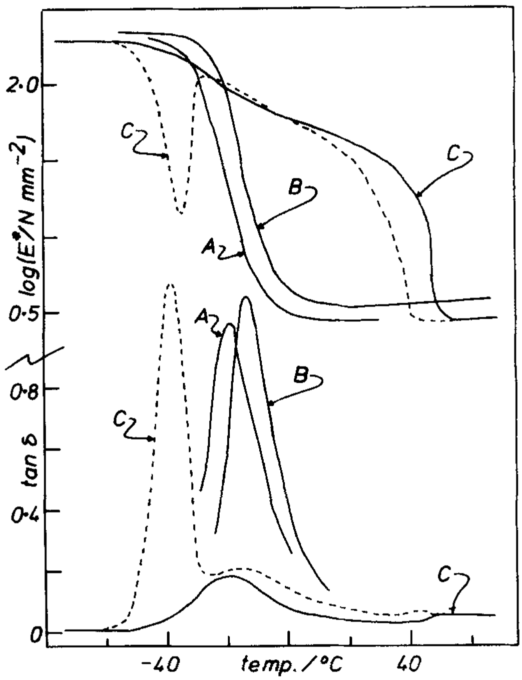

FIG. 6. Dynamic complex modulus and dynamic loss tangent curves as a function of temperature for samples with varying linking units. A, Sample 17 (TDI); B, Sample 20 (MDI); and C, Samples 21 annealed (full line) and 21Q quenched (broken line) (HDI). Only the transition regions of A and B are shown for clarity.

or above is extremely slow in all crystallizable samples; (2) in the DSC, none would crystallize in a decreasing temperature program of 20 K/min from above T_m to below T_g, whereas cold crystallization, i.e., crystallization in an increasing temperature program, occurs quite readily when the program commences at or about T_g, as shown by both Rheovibron and DSC experiments. T_g and T_m data for annealed and quenched forms of Samples 21, 31, and 33 are compared in Table 3.

Values of E* (~E') in both the glassy and rubbery regions of each polymer are given in Table 4. In the glassy region, E* is enhanced markedly by increasing the polycaprolactone segment length and less markedly by increasing the cross-link density. Replacing the aromatic linking units by HDI decreases E* in the glassy region. In the rubbery region E* is enhanced by having shorter polycaprolactone

TABLE 3. Melting and Glass Transition Temperatures of the Annealed and Quenched Forms of the Crystallizable Polymers by Rheovibron[a]

	Melting point (°K)		$(T_{max})_\delta$ (°K)	
Polymer	Annealed	Quenched	Annealed	Quenched
31	322	308	266	249
33	329	327	254	230
21	323	314	253	235

[a] The melting point of high MW annealed polycaprolactone homopolymer is reported to be 333 K [7].

TABLE 4. Complex Modulus Values in the Glassy and Rubbery Regions

Polymer		1	17	20	21Q	29	31Q	33Q
$E^*/N\ mm^{-2}$:	Glassy[a]	192	215	221	188	277	247	247
	Rubbery[b]	3.9	3.0	3.8	2.8	3.4	3.4	1.7

[a] E* at 203 K for all samples except Sample 1 for which it is at 213 K.

[b] E* at 333 K for all samples.

segment lengths or by the presence of the more rigid linking unit MDI and is decreased very significantly at low cross-link densities. It is not, however, enhanced by heavier cross-linking (compare Samples 29 and 31).

DISCUSSION

Previous work on the thermal properties of polyester-based-polyurethanes has been on linear (thermoplastic) types containing low MW diols or amines as chain extender. In the two-shot (prepolymer) process, the chain extender is added to the preformed diisocyanate-ended polyester at the final curing stage, whereas in the one-shot process all ingredients are reacted simultaneously. The morphology of the polymer can be made more complex by the presence of chain extender due to microphase separation into hard and soft segment domains. After certain thermal pretreatments, endothermic transitions, observed by thermal analysis in the lower temperature regions, have more recently been ascribed to soft segment, i.e., polyester segment, melting. For example, endotherms observed in the range 315 to 325 K for two-shot polyurethanes based on polyethylene adipate and aliphatic diisocyanates and cured with 1,4-butanediol were ascribed to polyester segment melting [7]. These had a hard segment content of 30 to 40 wt%. It is interesting to note that corresponding polyurethanes made from aromatic diisocyanates exhibited either a very small endotherm (TDI) or none at all (MDI) in this temperature region, although endotherms were observed at higher temperatures (400-480 K) due to hard segment melting. Thus, as in this work, the presence of aromatic linking agents tends to inhibit crystallization of the polyester segments. In previous work by Seefried, Koleske, and Critchfield on polycaprolactone-based, MDI-linked, linear polyurethanes containing 1,4-butanediol chain extender made by the one-shot method, crystallization similar to that observed in this work occurred in the sample containing polycaprolactone with MW 3130 but not in samples with lower MW [2]. In addition to the polycaprolactone MW, a relating factor influencing the ease of soft segment crystallization is undoubtedly the hard segment content. In the above work the crystallizable sample contained 16 wt% of hard segment while samples made from lower MW polycaprolactone contained 22 to 53 wt%. In the samples used in this study the hindrance to crystallization caused by the presence of cross-links would be balanced by the low hard segment concentration which ranged from 7 to 15 wt% for the crystallizable samples. The melting points of the annealed samples recorded in Table 3 are similar to that of the linear sample studied by Seefried et al. and all are in reasonable agreement with the reported value for high MW, annealed PCL homopolymer [8] (333 K) when it is considered that cross-linking or hard segment content must produce some disorder leading to greater imperfection in the crystalline regions.

The presence of crystalline material has a marked effect on the α-peak (the peak in the glass transition region of the mechanical loss curves). All the annealed forms of the crystallizable samples exhibited small broad α peaks with $(T_{max})_\delta$ values 17-24 K higher than the corresponding values for the quenched forms (see Table 3 and Figs. 4-6). Peaks and shoulders in curves for the corresponding quenched forms in the same temperature region are presumably due to the same transition in the newly formed semicrystalline polymer, i.e., just above the temperature of cold crystallization. High MW polycaprolactone [8] and polycaprolactone based linear polyurethanes [2] have also been observed to exhibit increases in T_g with crystallinity. The phenomenon has been particularly rigorously studied in polyethylene terephthalate [9] for which it has been observed that $(T_{max})_\delta$ increases with crystalline content in the lower crystallinity range but decreases again at higher crystallinity. Thus the complete explanation is complex. However, the increase is thought to be due to the crystalline regions locking the structure at various points, thereby reducing the effective length of the amorphous segments and consequently the segment flexibility. A similar explanation has been proposed for the observed decrease in T_g with increase in polyester MW, which was observed in this work and in other systems [10]. This trend is opposite to that generally observed for linear homopolymers [11], where the free chain ends lead to increased flexibility with a decrease in MW.

There has been a recent upsurge of interest in the theories of crystallization, in particular in the extent of motion that the molecule can undergo during the crystallization process [12]. Based on theoretical models, Flory and Yoon calculate that crystallization occurs with the minimum of motion while Di Marzio, Guttman, and Hoffman calculate that the forces of crystallization are sufficient to enable polymer molecules to be "reeled in" from the amorphous matrix in the available time. The latter view is compatible with the extensive adjacent reentry version of the folded chain model of crystal morphology, whereas the former is more compatible with the switchboard version. That crystallization can occur in the cross-linked polymers studied in this work shows that crystallization does not necessarily require the existence of free ends. Thus Flory and Yoon's model is the more realistic of the two in this case. However, this does not prove that the Di Marzio model is not applicable to other cases involving linear polymers.

ACKNOWLEDGMENTS

The work was carried out in the Department of Chemistry, University of Stirling, UK, where the author was on Study Leave, 1979.

The author is indebted to Dr L J. McEwen for valuable advice and assistance and to Dr G. B. Guise for supplying the polymer samples.

REFERENCES

[1] G. B. Guise and G. C. Smith, J. Appl. Polym. Sci., 25, 149 (1980).
[2] C. G. Seefried, J. V. Koleske, and F. E. Critchfield, Ibid., 19, 2493, 2503 (1975).
[3] R. A. Dunleavy and F. E. Critchfield, Rubber World, 156, 53 (1967).
[4] F. E. Critchfield, J. V. Koleske, and R. A. Dunleavy, Ibid., 164, 61 (1971).
[5] N. E. Rustad and R. G. Krawiec, Rubber Age, 105, 45 (November 1973).
[6] T. Murayama, Dynamic Mechanical Analysis of Polymeric Materials, Elsevier, Amsterdam, 1978, p. 21.

[7] R. R. Aitken and G. M. F. Jeffs, Polymer, 18, 197 (1977).
[8] J. V. Koleske and R. D. Lundberg, J. Polym. Sci., A2, 7, 795 (1969).
[9] Ref. 6, p. 67.
[10] K. Onder, R. H. Peters, and L. C. Spark, Polymer, 18, 155 (1977).
[11] J. M. G. Cowie, Polymers: Chemistry and Physics of Modern Materials, Intext Educational Publishers, New York, 1973, p. 220.
[12] Faraday Division, The Chemical Society, General Discussion No. 68, Cambridge, 1979.