

Secondary Relaxation, Brittle–Ductile Transition Temperature, and Chain Structure

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SYNOPSIS

We show that the subglass secondary relaxation temperature at which a polymer changes from brittle (crazing) to ductile (yielding) behavior is a function of the characteristic ratio C_∞ (which is a measure of the intrinsic flexibility and rigidity of a coiled chain). At 1 Hz frequency, the correlation is given by $\{T_\beta\}/\{T_\alpha\} = T_b/T_g = 0.135 + 0.082C_\infty$, where $\{T_\beta\}$ is the secondary relaxation temperature, which corresponds to T_b the brittle–ductile transition temperature, and $\{T_\alpha\}$ is the primary relaxation temperature, which corresponds to the glass transition temperature T_g at the given frequency. The ratio $\{T_\beta\}/\{T_\alpha\}$ or T_b/T_g can be predicted from chemical structure alone.

INTRODUCTION

It has long been recognized that the ductility (or toughness) of a polymer correlates in some way with secondary relaxation.^{1–16} Bohn and Oberst^{8–10} appeared to be the first to suggest such a correlation in their studies of impact toughness. Further studies by Heijboer,^{11,12} Boyer,¹³ Vincent,¹⁴ Baer and co-workers,^{5–7} and many others showed that the correlation is usually observed, but sometimes fails. This has led Heijboer¹² to state that “sometimes a polymer is brittle below and tough above the secondary relaxation.”

Of particular interest is the work of Baer and co-workers,^{5–7} who showed that the deformation and fracture behavior changes from brittle (crazing) below to ductile (yielding) above the secondary relaxation in polycarbonate, poly(ethylene terephthalate), and poly(2,6-dimethyl-1,4-phenylene oxide).

The accumulated results in the literature contain various aspects of the essential elements of the correlation and are perhaps best summarized by Wellinghoff and Baer,⁶ who concluded that “the presence of main-chain subglass secondary relaxation that is uncoupled from the internal motions of side groups is a common feature found in tough amor-

phous polymers.” The key words here are that the correlation exists, only when the subglass secondary relaxation is due to main-chain motions, not due to internal motions of side groups.

In this work we extend the salient results of the previous studies to identify the secondary relaxation that corresponds to the brittle–ductile transition, and establish a correlation among subglass secondary relaxation, brittle–ductile transition, and chain structure.

DEFINITIONS AND NOTATIONS

We designate the primary (glass) relaxation as the $\{\alpha\}$ transition at temperature $\{T_\alpha\}$, and the subglass secondary relaxation (which involves localized skeletal motions, decoupled from the internal motions of side groups) as the $\{\beta\}$ transition at temperature $\{T_\beta\}$. Notice that the curly brackets $\{\}$ are used here as an integral part of the present notations to distinguish them from the customary usage of Greek letters to denote the relaxations regardless of their molecular origins.^{1–4}

In the present notations, the glass transition is defined as the $\{\alpha\}$ relaxation, i.e.,

$$\{T_\alpha\} = T_g \quad (1)$$

where T_g is the glass transition temperature. The

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brittle-ductile transition is defined as the $\{\beta\}$ relaxation, i.e.,

$$\{T_\beta\} = T_b \quad (2)$$

where T_b is the brittle-ductile transition temperature at which a polymer glass changes from brittle (crazing) to ductile (yielding) behavior in deformation and fracture at a given frequency, shown by Baer and co-workers⁵⁻⁷ and others.^{1-4,8-16}

Let us exclude all the apparent secondary relaxations that arise from internal stresses, absorbed water, plasticizers, and the motions in crystalline domains and domain boundaries. We then have the following relationships.

In amorphous polymers, $\{\alpha\}$ relaxation usually corresponds to the customary α relaxation, which is the glass transition, i.e.,

$$\{T_\alpha\} = T_\alpha = T_g \quad (\text{amorphous polymers}) \quad (3)$$

and $\{\beta\}$ relaxation usually corresponds to the customary β relaxation, which is the brittle-ductile transition, i.e.,

$$\{T_\beta\} = T_\beta = T_b \quad (\text{amorphous polymers}) \quad (4)$$

Exceptions to this rule will arise, when brittle-ductile transition is sufficiently close to and merges with glass transition. In this case the $\{\beta\}$ transition is not discernible in the relaxation spectrum, and a different secondary relaxation that appears below the merged peak would then be identified as the customary β transition, which is, of course, not our $\{\beta\}$ transition. An example is poly(cyclohexyl methacrylate), discussed further later.

In semicrystalline polymers, such as polyethylenes,^{3,17} the customary α transition is usually due to motions in the crystalline domains and/or domain boundaries, and the customary β relaxation is the glass transition. Therefore, the $\{\alpha\}$ relaxation usually corresponds to the customary β relaxation, i.e.,

Table I Relaxation Temperatures and Characteristic Ratio for Some Polymers

Polymer	$\{T_\alpha\}$, K at 1 Hz	$\{T_\beta\}$, K at 1 Hz	$\{T_\beta\}/\{T_\alpha\}$	Method ^a	C_α ^b	References ^c
PSO	459	169	0.37	M	2.2	22-24
PC	428	163	0.38	M	2.4	25-29
PAT	471	180	0.38	M, D	2.6	30, 31
PAR50	472	185	0.39	M	3.1	29, 31, 32
PPO	493	158	0.32	M, D	3.2	32-35
PAR70	466	187	0.41	M	3.3	29, 31, 32
PEIM	485	171	0.35	M	3.6	36, 37
PAI	457	187	0.41	M, D	3.7	29, 31, 32
PET	355	200	0.56	M	4.1	26, 31, 38
PE	275	165	0.60	M	5.7	39-41
N66	341	208	0.61	M	6.1	31, 38
POM	260	203	0.78	M	7.5	31, 38, 42-44
sPMMA	403	313	0.78	M	7.6	45
cPMMA	395	302	0.75	M, D	7.9	46-48
PMMA/DBP5	373	308	0.83	D	8.1	31, 49
PMMA/DBP10	363	308	0.85	D	8.3	31, 49
PEMA	362	300	0.83	M	8.4	46
PnPMA	332	300	0.90	M	8.8	46
PMMA/DBP25	355	308	0.87	D	9.1	31, 39
PnBMA	307	293	0.95	M	9.2	46
iPMMA	373	342	0.92	M	10.7	45
PS	373	363 ^d	0.97	M	10.8	31, 50
PCyHMA	406	406	~ 1	M	11.6	46, 51
PtBMA	395	395	~ 1	M	12.0	46
PPhMA	407	407	~ 1	M	13.0	46

^a M refers to dynamic mechanical method, D refers to dielectric relaxation method.

^b All C_α data are taken from Ref. 20.

^c References are the data sources for $\{T_\alpha\}$, $\{T_\beta\}$, T_g , or T_b .

^d By tensile test, see Ref. 50.

$$\{T_\alpha\} = T_\beta = T_g \quad (\text{semicrystalline polymers}) \quad (5)$$

and the $\{\beta\}$ relaxation usually corresponds to the customary γ relaxation, which is the brittle-ductile transition, i.e.,

$$\{T_\beta\} = T_\gamma = T_b \quad (\text{semicrystalline polymers}) \quad (6)$$

CORRELATION OF SECONDARY RELAXATION TEMPERATURE WITH CHAIN STRUCTURE

We have previously shown that the yield stress σ_y is a function of the characteristic ratio C_∞ , which is a measure of the intrinsic flexibility and rigidity of a chain, i.e.,¹⁸

$$\sigma_y \propto C_\infty \quad (7)$$

We have previously redefined Flory's characteristic ratio of a coiled chain by¹⁸⁻²⁰

$$C_\infty = \lim_{n_v \rightarrow \infty} \frac{\langle R_0^2 \rangle}{n_v \langle l_v^2 \rangle} \quad (8)$$

where $\langle R_0^2 \rangle$ is the mean-square end-to-end distance of an unperturbed chain, n_v the number of real and/or virtual skeletal bond, which is an elementary conformational rotational unit, and $\langle l_v^2 \rangle$ the mean-

square length of a real or virtual skeletal bond, discussed in detail elsewhere.²⁰ When defined this way, C_∞ is a measure of the intrinsic flexibility and rigidity of a coiled chain.

Since $\{T_\beta\}$ corresponds to T_b the brittle-ductile transition temperature, we thus expect that the ratio $\{T_\beta\}/\{T_\alpha\}$ should be a function of the intrinsic flexibility and rigidity of a chain, i.e., the characteristic ratio.

Table I lists the values of $\{T_\alpha\}$, $\{T_\beta\}$, and $\{T_\beta\}/\{T_\alpha\}$ at 1 Hz, and C_∞ for a variety of coiled-chain polymers. The acronyms for the polymers are identified at the end of the text. The symbol M stands for dynamic mechanical method, and the symbol D stands for dielectric relaxation method, used in determining the transition temperatures. Least-squares regression gives

$$\frac{\{T_\beta\}}{\{T_\alpha\}} = \frac{T_b}{T_g} = (0.135 \pm 0.027) + (0.082 \pm 0.004)C_\infty \quad (9)$$

where $\{T_\alpha\}$ and $\{T_\beta\}$ are the values at 1 Hz, and when $C_\infty > \sim 10.5$, we have $\{T_\beta\}/\{T_\alpha\} = T_b/T_g = 1$.

Figure 1 plots the ratio $\{T_\beta\}/\{T_\alpha\}$ versus C_∞ . The symbols are experimental; the solid line is drawn to Eq. (9). This figure indeed confirms that the ratio $\{T_\beta\}/\{T_\alpha\}$ is a function of C_∞ .

The relaxation temperatures $\{T_\alpha\}$ and $\{T_\beta\}$ are

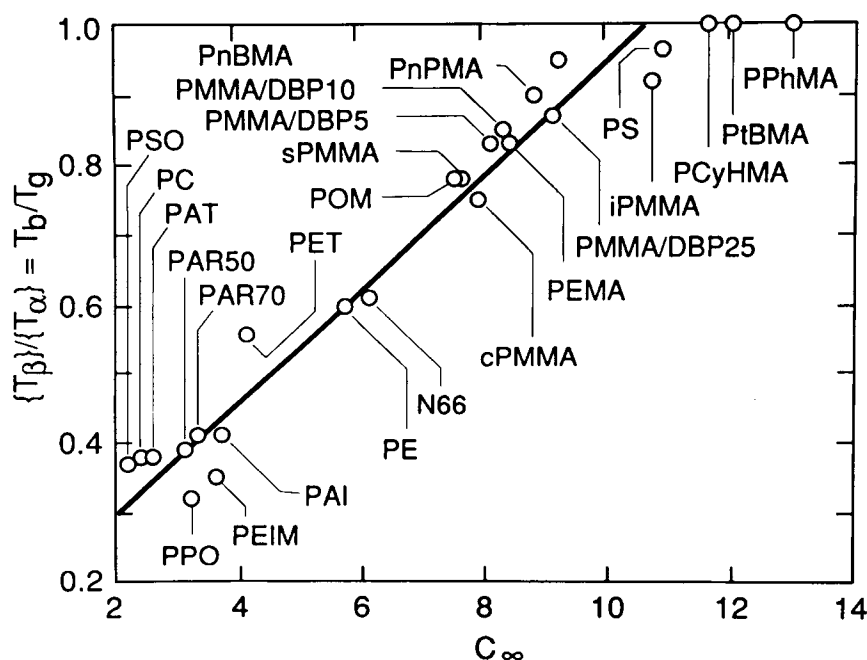


Figure 1 $\{T_\beta\}/\{T_\alpha\} = T_b/T_g$ values at 1 Hz versus C_∞ for some coiled-chain polymers.

Table II Frequency Dependence of $\{T_\beta\}/\{T_\alpha\}$

Polymer	E_α (kcal/mol)	E_β (kcal/mol)	$\{T_\beta\}/\{T_\alpha\}$		
			1 Hz	10 Hz	100 Hz
PPO	150 ^a	8.7 (a)	0.30	0.32	0.34
cPMMA	105 ^b	19 (b)	0.76	0.81	0.86

^a F. E. Karasz, W. J. MacKnight, and J. Stoelting, *J. Appl. Phys.*, **41**, 4357 (1970).

^b N. G. McCrum, B. E. Read, and G. Williams, *Anelastic and Dielectric Effects in Polymeric Solids*, Wiley, New York, 1967.

frequency dependent, given by the Arrhenius equation⁴,

$$f = A \exp\left(\frac{-E}{RT}\right) \quad (10)$$

where f is the frequency, A the prefactor, E the activation energy, R the gas constant, and T the temperature. We thus have

$$\frac{\{T_\beta\}}{\{T_\alpha\}} = \left(\frac{E_\beta}{E_\alpha}\right) \left[\frac{\log(f/A_\alpha)}{\log(f/A_\beta)}\right] \quad (11)$$

Table II lists the dependence of $\{T_\alpha\}$ and $\{T_\beta\}$ on frequency for poly(2,6-dimethyl-1,4-phenylene oxide) ($E_\alpha = 150$ kcal/mol, $E_\beta = 8.7$ kcal/mol, $A_\alpha = 1.22 \times 10^{66}$ Hz, and $A_\beta = 6.03 \times 10^{10}$ Hz), and conventional poly(methyl methacrylate) ($E_\alpha = 105$ kcal/mol, $E_\beta = 19$ kcal/mol, $A_\alpha = 3.69 \times 10^{56}$ Hz, and $A_\beta = 3.02 \times 10^{13}$ Hz).

Figure 2 shows the variation of the ratio $\{T_\beta\}/\{T_\alpha\}$ with frequency. It can be seen that the frequency dependency is not very large within, say, one-decade change in the frequency, and should not af-

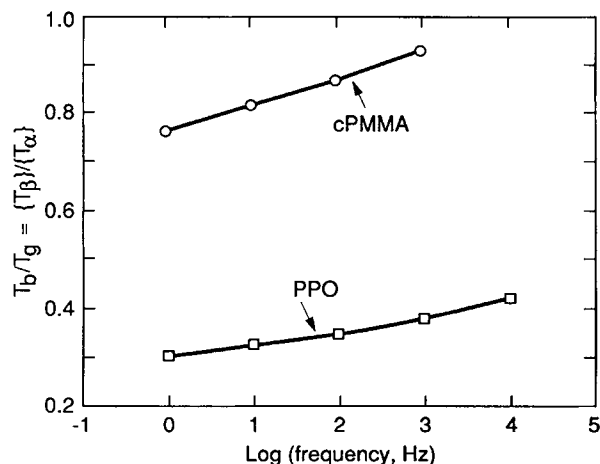


Figure 2 $\{T_\beta\}/\{T_\alpha\} = T_b/T_g$ values versus frequency for cPMMA and PPO.

fect the essence of the correlation. Numerical values of the coefficients in Eq. (9) will change with frequency, but the essential nature of the correlation, i.e., the functional form remains the same.

DISCUSSION

Previously, Boyer⁵² reported that $\{T_\beta\}/\{T_\alpha\} \approx 0.75$ at 100 Hz for polymers with C-C and C-O main chains (skeletal bonds), which are free of long alkyl and alkoxy side groups. We note that such chains have $C_\infty \approx 8$, and thus $\{T_\beta\}/\{T_\alpha\} \approx 0.75$, as indeed predicted by Eq. (9).

The "maximum" ductility is attained when $C_\infty = 2$ for chains with tetrahedral skeletal bonds.¹⁸ Therefore, Eq. (9) predicts $\{T_\beta\}/\{T_\alpha\} = T_b/T_g = 0.3$ as the lowest possible value for such chains. In other words the "maximum" ductility in chains with tetrahedral skeletal bonds occurs, when $C_\infty = 2$ and $\{T_\beta\}/\{T_\alpha\} = T_b/T_g = 0.3$. On the other hand, chains having $C_\infty > \sim 10.5$ will have $\{T_\beta\} = \{T_\alpha\}$, or $T_b = T_g$.

The molecular origins of secondary relaxations are usually suggested indirectly based on inferential evidence. Therefore, they are subject to diverse and conflicting views.¹⁻⁴ However, it is interesting to note that both the ratio $\{T_\beta\}/\{T_\alpha\}$ and the yield stress σ_y correlate with C_∞ , which is a measure of the intrinsic flexibility and rigidity of a chain. The onset of yielding in the glassy region sufficiently far (say, 10–15°C) below the glass transition has been shown to arise from the onset of skeletal bond rotation under the applied stress.^{18,53-57} Therefore, the $\{\beta\}$ transition and the brittle-ductile transition should involve certain localized skeletal motions that enable

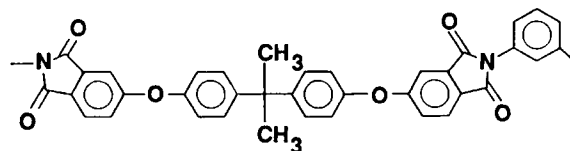


Figure 3 Chemical structure of PEIM.

the onset of yielding. This is consistent with the theoretical analysis of Ryzhov and Byershtein,⁵⁸ who showed that the customary β relaxation arises from torsional skeletal motions of about five skeletal units in vinyl, acrylic, oxyalkylene, and silicone chains.

The ratio $\{T_\beta\}/\{T_\alpha\} = T_b/T_g$ relates to the onset of yielding (i.e., the yield point), which arises from the onset of conformational rotation of skeletal bonds under the applied stress. Macroscopically, the onset of yielding occurs when the yield stress σ_y is lower than the crazing stress σ_z .¹⁸ Therefore, the ratio $\{T_\beta\}/\{T_\alpha\}$ relates to whether a polymer tends to craze (brittle behavior) or yield (ductile behavior).¹⁸ On the other hand, the degree of ductility (toughness) relates to the post-yield process of cold drawing, which involves different molecular mechanisms, i.e., alignment and sliding of chains past one another.

It is tempting to correlate the size of $\{\beta\}$ relaxation peak with the degree of ductility (or toughness). However, it has been shown that the size of secondary relaxation peak is determined by the difference between unrelaxed and relaxed moduli.¹⁷ Therefore, neither the size of $\{\beta\}$ relaxation peak nor the ratio $\{T_\beta\}/\{T_\alpha\}$ is a measure of the degree of ductility (toughness).

In polystyrene, poly(*t*-butyl methacrylate), poly(phenyl methacrylate), and poly(cyclohexyl methacrylate), the brittle-ductile transition occurs near the glass transition, i.e., $\{T_\beta\} = T_b \approx T_g$, as found by static tensile tests.^{7,14} Therefore, in these polymers, the $\{\beta\}$ transition merges with the glass transition and is not detectable in the dynamic or dielectric relaxation spectra. Consequently, the customary β transitions observed in these polymers, such as the weak customary β relaxation at about 313 K in polystyrene,⁵⁹ are not the $\{\beta\}$ transitions. They are probably due to the motions of side groups, not involving the main chain. Furthermore, the customary β transition at about 193 K in poly(cyclohexyl methacrylate) has been shown to be due to the chair-chair conformational transformation of cyclohexyl side group.¹⁵

CONCLUSION

We have shown that the subglass $\{\beta\}$ transition temperature $\{T_\beta\}$, which corresponds to brittle-ductile transition temperature T_b , is controlled by the characteristic ratio C_∞ , which is a measure of the intrinsic flexibility and rigidity of a coiled chain. We have previously shown that C_∞ values can be predicted from chemical structure.²⁰ Therefore, the ratio $\{T_\beta\}/\{T_\alpha\}$ or T_b/T_g can be predicted from chemical structure alone.

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LIST OF ACRONYMS

N66	Poly(hexamethylene adipamide), nylon 66
PAI	Polyarylate of bisphenol A and isophthalic acid
PAR50	Polyarylate of bisphenol A (1 mol), isophthalic acid (0.5 mol) and terephthalic acid (0.5 mol)
PAR70	Polyarylate of bisphenol A (1 mol), isophthalic acid (0.7 mol) and terephthalic acid (0.3 mol)
PAT	polyarylate of terephthalic acid
PnBMA	Poly(<i>n</i> -butyl methacrylate)
PtBMA	Poly(<i>t</i> -butyl methacrylate)
PC	Polycarbonate of bisphenol A
PCyHMA	Poly(cyclohexyl methacrylate)
PE	Polyethylene
PEIM	Polyetherimide, see Figure 3 for chemical structure
PEMA	Poly(ethyl methacrylate)
PET	Poly(ethylene terephthalate)
cPMMA	Conventional poly(methyl methacrylate), free-radical polymerized
iPMMA	Isotactic poly(methyl methacrylate)
sPMMA	Syndiotactic poly(methyl methacrylate)
PMMA/DBP5	Poly(methyl methacrylate) plasticized with 5% dibutylphthalate
PMMA/DBP10	Poly(methyl methacrylate) plasticized with 10% dibutylphthalate
PMMA/DBP25	Poly(methyl methacrylate) plasticized with 25% dibutylphthalate
POM	Polyoxymethylene
PnPMA	Poly(<i>n</i> -propyl methacrylate)
PPhMA	Poly(phenyl methacrylate)
PPO	Poly(2,6-dimethyl-1,4-phenylene oxide)
PS	Conventional polystyrene
PSO	Polysulfone of bisphenol A and diphenylenesulfone

REFERENCES

1. A. J. Kinloch and R. J. Young, *Fracture Behavior of Polymers*, Applied Science Publishers, London, 1983.
2. L. E. Nielsen, *Mechanical Properties of Polymers and Composites*, Volumes 1 and 2, Marcel Dekker, New York, 1974.
3. I. M. Ward, *Mechanical Properties of Solid Polymers*, 2nd ed., Wiley, New York, 1971.
4. N. G. McCrum, B. E. Read, and G. Williams, *Anelastic and Dielectric Effects in Polymeric Solids*, Wiley, New York, 1967.
5. J. R. Kastelic and E. Baer, *J. Macromol. Sci. Phys.*, **B 7**, 679 (1973).
6. S. T. Wellinghoff and E. Baer, *J. Appl. Polym. Sci.*, **22**, 2025 (1978).
7. K. Matsushige, S. V. Radcliff, and E. Baer, *J. Appl. Polym. Sci.*, **20**, 1853 (1976).
8. L. Bohn and H. Oberst, *Acustica*, **9**, 431 (1959).
9. H. Oberst, *Kunststoffe*, **53**, 4 (1963).
10. L. Bohn, *Kunststoffe*, **53**, 826 (1963).
11. J. Heijboer, *J. Polym. Sci. Symp.*, **C 16**, 3755 (1968).
12. J. Heijboer, in *Molecular Basis of Transitions and Relaxations*, D. J. Meier, Ed., Gordon and Breach, London, 1978, pp. 75-102.
13. R. F. Boyer, *Polym. Eng. Sci.*, **8**, 161 (1968).
14. P. I. Vincent, *Polymer*, **1**, 425 (1960).
15. J. Heijboer, in *Molecular Basis of Transitions and Relaxations*, D. J. Meier, Ed., Gordon and Breach, London, 1978, pp. 297-310.
16. M. G. Wyzgoski and G. S. Y. Yeh, *J. Macromol. Sci. Phys.*, **B 10**, 441 (1974).
17. R. H. Boyd, *Polymer*, **26**, 323 (1985); **26**, 1123 (1985).
18. S. Wu, *Polym. Eng. Sci.*, **30**, 754 (1990).
19. S. Wu, *J. Polym. Sci. B. Polym. Phys.*, **27**, 732 (1989).
20. S. Wu, *Polym. Eng. Sci.*, **32** (1992).
22. L. M. Robeson, A. G. Farnham, and J. E. McGrath, in *Molecular Basis of Transitions and Relaxations*, D. J. Meier, Ed., Gordon and Breach, London, 1978, pp. 405-425; *Appl. Polym. Symp.*, **26**, 373 (1975).
23. J. R. Fried, A. Letton, and W. J. Welsh, *Polymer*, **31**, 1032 (1990).
24. M. Baccaredda, E. Butta, V. Frosini, and S. de Petris, *J. Polym. Sci. Polym. Phys.*, **5**, 1296 (1967).
25. F. P. Reding, J. A. Faucher, and R. D. Whitman, *J. Polym. Sci.*, **54**, 556 (1961).
26. J. R. Kastelic and E. Baer, *J. Macromol. Sci.-Phys.*, **B 7**, 679 (1973).
27. K. H. Illers and H. Breuer, *Kolloid Z.*, **176**, 110 (1961).
28. K. H. Illers and H. Breuer, *J. Colloid Sci.*, **18**, 1 (1963).
29. J. Bussink and J. Heijboer, in *Physics of Non-Crystalline Solids*, J. A. Prins, Ed., North Holland Publishing, Amsterdam, 1965, pp. 388-396.
30. G. P. Mikhailov and M. P. Eidelnant, *Vysokomol. Soedin.*, **2**, 287 (1960).
31. N. G. McCrum, B. E. Read, and G. Williams, *Anelastic and Dielectric Effects in Polymeric Solids*, Wiley, New York, 1967.
32. This work.
33. F. E. Karasz, W. J. MacKnight, and J. Stoelting, *J. Appl. Phys.*, **41**, 4357 (1970).
34. J. Heijboer, *J. Polym. Sci., C* **16**, 3755 (1968).
35. J. Stoelting, F. E. Karasz, and W. J. MacKnight, *Polym. Eng. Sci.*, **10**, 133 (1970).
36. J. E. Harris and L. M. Robeson, *J. Appl. Polym. Sci.*, **35**, 1877 (1988).
37. M. I. Bessonov, *Polyimidy-Klass Termostoykikh Polimerov*, Nauka Press, Leningrad, 1983, Chapter 3.6.
38. M. Takayanagi, *Memo. Faculty Eng. Kyushu Univ.*, **23**(1), 1 (1963).
39. D. E. Kline, J. A. Sauer, and A. E. Woodward, *J. Polym. Sci.*, **22**, 455 (1956).
40. K. H. Illers, *Kolloid Z. Z. Polym.*, **251**, 394 (1973).
41. R. H. Boyd, *Macromolecules*, **17**, 903 (1984).
42. N. G. McCrum, *J. Polym. Sci.*, **54**, 561 (1961).
43. L. Bohn, *Kolloid Z.*, **201**, 20 (1965).
44. R. H. Boyd, *Polymer*, **26**, 323 (1985).
45. G. P. Mikhailov and T. I. Borisova, *Polym. Sci. USSR*, **2**, 387 (1961).
46. J. Heijboer, in *Physics of Non-Crystalline Solids*, North Holland, Amsterdam, 1965, pp. 231-254.
47. J. Heijboer, in *Molecular Basis of Transitions and Relaxations*, D. J. Merier, Ed., Gordon and Breach, London, 1978, pp. 75-102.
48. J. Heijboer, in *Molecular Basis of Transitions and Relaxations*, D. J. Merier, Ed., Gordon and Breach, London, 1978, pp. 297-310.
49. G. P. Mikhailov, T. I. Borisova, and D. A. Dmitrochenko, *J. Tech. Phys. (USSR)*, **26**, 1924 (1956).
50. K. Matsushige, S. V. Radcliff, and E. Baer, *J. Appl. Polym. Sci.*, **20**, 1853 (1976).
51. P. I. Vincent, *Plastics (London)*, **26**(11), 141 (1961); **27**(1), 115 (1962).
52. R. F. Boyer, *J. Polym. Sci. Symp.*, **C 50**, 189 (1975).
53. J. F. Jansson and I. V. Yannas, *J. Polym. Sci. B. Polym. Phys.*, **15**, 2103 (1977).
54. I. M. Ward, *Polym. Eng. Sci.*, **24**, 724 (1984).
55. I. J. Hutchinson, I. M. Ward, H. A. Willis, and V. Zichy, *Polymer*, **21**, 55 (1980).
56. B. Armram, L. Bokobza, L. Monnerie, and J. P. Queslel, *Polymer*, **29**, 1155 (1988).
57. Y. Abe and P. J. Flory, *J. Chem. Phys.*, **52**, 2814 (1970).
58. V. A. Ryshov and V. A. Byershtein, *Polym. Sci. (USSR)*, **31**, 496 (1989).
59. R. F. Boyer and S. G. Turley, in *Molecular Basis of Relaxations and Transitions*, D. J. Meier, Ed., Gordon and Breach, London, 1978, pp. 333-358.

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