

CARBON-13 NMR RELAXATION PARAMETERS OF SEMI-CRYSTALLINE POLYMERS

Leo Mandelkern

Department of Chemistry and Institute of Molecular Biophysics, Florida State University, Tallahassee, Florida 32306, USA

Abstract - The studies of the carbon-13 nmr relaxation parameters, under conditions of scalar proton decoupling, are shown to be effective in the investigation of properties of the non-crystalline regions of semi-crystalline polymers. A review is given of the influence of structure and morphology on these parameters, and a semi-quantitative assessment made of different contributions to the resonant line width. The application of these methods to further the understanding of glass formation and other transitions in semi-crystalline polymers will be presented.

INTRODUCTION

Studies of carbon-13 nmr relaxation parameters can be used for the analysis of the segmental motions and structure of bulk polymers (1)(2)(3). Sophisticated and very fruitful methods involving dipolar decoupling, magic angle spinning and cross-polarization, have been developed to study glasses and the internal structure of the crystalline regions in polymers (4)(5)(6). Scalar proton decoupling measurements have also proven capable of yielding high resolution spectra for pure undiluted amorphous polymers as well as for the non-crystalline regions of semi-crystalline polymers well above the respective glass temperatures (2)(3)(7)(8). The major portion of the work which we shall be discussing will be restricted to the scalar decoupling technique. We shall, however, report some initial studies involving high power (dipolar) decoupling, independent of as well as in conjunction with magic angle spinning. These results complement the main work presented.

The motivation for using carbon-13 nmr techniques in our laboratory has been to ascertain what additional information could be gained with respect to a specific set of polymer problems in which we have been interested. These include the properties of the non-crystalline regions of semi-crystalline polymers, the nature of glass formation and the secondary transitions associated with crystalline polymers. An example of the latter would be the beta transition of the polyethylenes and related copolymers. In the studies of the semi-crystalline polymers we are interested in what relations exist, if any, between the quantities which describe the crystallinity of the sample and the molecular constitution of the system on the one hand and the nmr relaxation parameters, such as the spin-lattice relaxation time, T_1 , the nuclear Overhauser enhancement, NOE, and the line width $\nu_{1/2}$, on the other. Hence we will be concerned, in the main, with samples that have been well characterized with respect to the degree of crystallinity, supermolecular structure, or crystalline morphology, molecular weight and distribution and degree of branching. It is now known that a wide range in the level of crystallinity and type of supermolecular organization can be achieved in many semi-crystalline polymers (9)(10)(11). Hence these variables have to be controlled for meaningful interpretations to result. The work being presented thus represents a series of interrelated projects with major collaborators. These collaborators, Drs. R.A. Komoroski, D.E. Axelson, J.J. Dechter and A.H. Dekmezian have each made rather significant independent contributions to the work being summarized here. These contributions are gratefully acknowledged.

RELAXATION PARAMETERS OF PURE UNDILUTED SEMI-CRYSTALLINE POLYMERS

Spin-lattice relaxation - T_1

We shall consider first the influence of the level of crystallinity and crystalline morphology on T_1 for semi-crystalline polymers. Before detailing the results we can summarize the evidence by stating that in a series of controlled experiments with natural rubber (*cis* polyisoprene) (12) a wide variety of linear and branched polyethylenes (3)(7)(13), polyethylene oxide (3) and polytrimethylene oxide (3) the T_1 's were found to be quite insensitive to either crystallization or molecular parameters. For example, the T_1 's are independent of the level of crystallinity, the fact whether the sample is crystalline at all, the

supermolecular structure, whether crystallization is carried out in the pure state (bulk) or from dilute solution, the molecular weight, molecular weight distribution or branching concentration.

More specifically, a direct comparison of T_1 's can be made, at the same temperature between completely amorphous and partially crystalline cis polyisoprene (12). This definitive experiment could be carried out because the rate of crystallization is relatively slow for this polymer. The limitation that is imposed is that only about a 30 percent level of crystallinity can be attained. In Table 1 we have compared the T_1 's of each of the five carbons for the completely amorphous polymer with the semi-crystalline one, with a degree of crystallinity $1-\lambda = 0.30$.

TABLE 1. Carbon-13 T_1 (ms) for cis-polyisoprene at 0°C and 67.9 MHz (12)

Carbon	Amorphous	Semi-Crystalline ^(a)
α	2000	2400
β	400	460
γ	260	270
δ	240	270
ϵ	840	910

(a) Degree of crystallinity $1-\lambda = 0.3$

It is quite clear from the data in Table 1 that the T_1 's for each of the individual carbons in this repeating unit is invariant with crystallinity. It has not been possible to make this comparison with the amorphous state at higher levels of crystallinity, and to take into account any influence of supermolecular structure at a constant temperature in any practical experiment. It then becomes necessary to determine this parameter as a function of crystallinity, superstructure and temperature into the melt. An extensive set of such measurements have been made with the polyethylenes (7)(13). In Table 2 we list a typical set of T_1 values at a fixed temperature, 45°C, for a variety of fractionated and unfractionated polyethylenes having different molecular weights, levels of crystallinity and supermolecular structures.

TABLE 2. Carbon-13 T_1 (ms) for linear polyethylenes at 45°C and 67.9 MHz (13)

M_n	$1-\lambda$	Morphology	T_1
8.1×10^4	0.57	Spher.	343
2.5×10^5	0.51	Spher.	355
1.7×10^5	0.81	Spher.	348
2.0×10^6	0.51	None	369
2.0×10^6	0.72	None	358
$2.7_5 \times 10^4$	0.94	Rod	352

The molecular weight clearly has no influence on T_1 for the semi-crystalline polymer. The very large range in the degree of crystallinity, the optimum that can be achieved for linear polyethylene at ambient temperature, does not alter this quantity. It is also independent of the different types of supermolecular structures that can be achieved for linear polyethylene (3)(7)(13), or if a well organized or well defined structure can be found at all. The "none" in Table 2 indicates a collection of lamella-like crystallites randomly arranged relative to one another (9).

The T_1 values for the backbone carbons of the branched polyethylenes are the same as the linear counterpart and both type samples display the same temperature dependence (7)(13). As would be expected, T_1 is an increasing function of temperature and there is no difference between the different bulk crystallized samples. T_1 is also a continuous function of temperature through the melting temperature and into the molten state (3)(7)(13). Very similar molecular weight and temperature behavior is also found for poly(ethylene oxide) and poly(trimethylene oxide). We can conclude from these observations that T_1 in the non-crystalline regions of these polymers is the same as that of the pure melt (amorphous polymer). This is the same conclusion reached by direct comparison with cis-polyisoprene and would thus seem to be of general validity.

When precipitated from dilute solution homopolymers form crystallites which yield a characteristic platelet habit (14) which at one time was thought to have a regularly folded interfacial structure. T_1 values, as a function of temperature, can be obtained for such crystalline systems (15). Since only scalar decoupling is used carbons within the interior

of the crystal can not be observed and the motion of carbons in the interfacial region are those being studied. The values determined for T_1 , on the other hand, are the same as those for the amorphous regions of melt crystallized polymer of varying degrees of crystallinity (Table 2). The identity of T_1 for solution and bulk crystallized polymers must reflect the same type of chain-structure in the non-crystalline regions for both cases. These results are obviously not in accord with the postulated highly ordered, regularly structured interface for solution formed crystals. They agree with the conclusion from other physical measurements (16) and have important implications to the details of the interfacial structure (16).

Based on the extensive results that have been obtained, for several different polymer types, we find that the T_1 's are independent of all aspects of structure that describe crystallinity. We thus conclude that the relatively fast segmental motions, as manifested in T_1 , are independent of these factors and are the same for the completely amorphous polymer at comparable temperatures. For semi-crystalline polyethylene it can also be shown that the correlation time associated with these motions is essentially the same as the interior carbons of molten n -alkanes (13).

Nuclear Overhauser enhancement

The influence of the crystallinity parameters on the nuclear Overhauser enhancement (NOE) has not as yet been studied in as much detail as has either the spin-lattice parameter or line width. However, some interesting preliminary results have been obtained which suggest that potentially useful information can be developed from this quantity. For natural rubber, the NOE's for each of the carbons are very low in the amorphous state. Therefore, the fact that virtually no change is observed upon crystallization for this polymer is to be expected (12).

Both linear and branched polyethylenes, in the molten state, have full NOE's of three (3)(13) (17). Polyethylene oxide yields the same result (3). Surprisingly the full NOE is maintained at ambient temperatures for these semi-crystalline polymers when the level of crystallinity is as high as 50 percent. The relatively limited amount of data that has been obtained so far for linear polyethylene at ambient temperature is given in Table 3. Although

TABLE 3. Nuclear Overhauser enhancement for linear polyethylene at 45°C and 67.9 Hz (13)

M_n	Morphology	$1-\lambda$	NOE
2.0×10^6	None	0.51	3.0
2.5×10^5	Spher.	0.51	3.0
1.7×10^5	Spher.	0.81	2.5
2.75×10^4	Rod	0.94	2.0

the data available at present is admittedly limited there is the suggestion that the NOE is dependent on the level of crystallinity, irrespective of the crystalline morphology. It would appear that as the level of crystallinity increases above 0.50 the NOE decreases. More extensive data is of course needed to firmly establish this point. It would be helpful if another semi-crystalline system, where a much larger range in the level of crystallinity could be attained, were studied. We should note that since T_1 is independent of the level of crystallinity for polyethylene, the NOE results in Table 3 imply a change in the distribution of correlation times and the average correlation time, for the non-crystalline methylene carbons, as the level of crystallinity is increased above 0.50.

Line width

In discussing the scalar decoupled resonant line widths that are obtained for polyethylene it is convenient to consider separately the results in the completely molten state and in the semi-crystalline state. The T_1 and NOE values for molten polyethylene indicate rapid segmental motion which can be described by a single correlation time (3)(12). Poly(ethylene oxide) in the melt yields a similar conclusion. Consequently, relatively narrow resonant line widths, the order of 0.1 Hertz would be expected in the melt at a magnetic field strength of 67.9 MHz. Allowing for reasonable experimental error, one might then expect to observe line widths the order of several Hertz. In contrast to this expectation, we had in fact reported that the line widths were the order of several hundred Hertz for high molecular weight polyethylene and polyethylene oxide in the melt (3)(7)(12). We now know that these results were not correct. These initial results were in the main a consequence of improper sample preparation and, to a somewhat lesser extent, magnetic field homogeneity at the higher temperatures (7). The matter of sample preparation should be important to all polymer systems and presents a rather practical but very important problem. It is important that the sample be in some sort of continuum form; i.e. as solid a geometric form as possible. The use of pellets, films and powders, admittedly very convenient, is not good practice, and as

the data in Table 4 will indicate is the reason for the very large line widths originally reported. This requirement imposes many practical problems, particularly for high molecular weight polymers, since samples can not be rejected or accepted merely by visual inspection. Severe limitations are also placed on the structural and morphological variables that can be studied (7). Examples of the line widths that can be attained, when extreme care is taken, are given in Table 4 for linear polyethylenes of differing molecular weights at 140°C at two

TABLE 4. Line width at 140°C for linear polyethylene (7)

Polymer	$M_N \times 10^{-4}$	$M_w \times 10^{-5}$	Line Width $\nu_{1/2}$	
			67.9 MHz	22.6 MHz
C ₉₄ H ₁₉₀	0.13	0.013	4	
LPE-1	0.11	0.013	6	0.8
LPE-2	0.18	0.020	4	
LPE-3 ^(a)		0.086 ^(b)	11	
LPE-4	0.18	0.52	11	3.2
LPE-5	1.2	1.5	18	5.6
LPE-6		20 ^(b)	35	6.8

(a) Molecular weight fraction

(b) Viscosity average molecular weight

magnetic field strengths. Similar results are obtained for comparable branched samples (7). We can note immediately that with proper sample preparation and field homogeneity a substantial reduction in the 67.9 MHz line width is achieved relative to that reported previously (3)(12). On examining this new data closely, it would appear that the line widths increase with increasing molecular weight. This result is probably more apparent than real. It could very easily represent the ever-increasing difficulty in preparing proper samples with increasing molecular weight because of the increasing melt viscosity. One of the requirements is to have as bubble-free a sample as is possible. This requirement is difficult to achieve with laboratory facilities for very high molecular weights. Prudence, therefore, dictates that the values listed for the line width should only be taken as upper limits, particularly for the high molecular weight samples. This problem, which should be of concern for all pure (undiluted) polymer systems, will make difficult detailed interpretations of the line width. We must therefore recognize that there is an inherent problem in sample preparation which is going to make it very difficult to decide when optimum conditions are achieved.

The data in Table 4 also demonstrates that in the melt the line width has a definite field dependence. The ratio of the widths at the two fields is about four. We estimate that the field independent line widths are the order of one to three Hertz in the melt (7). This result then makes for a much more compatible set of parameters between T_1 , NOE and $\nu_{1/2}$. The small, limiting values of the (field independent) line widths are probably due to inhomogeneities in the static magnetic field and are not the natural T_2 .

Upon crystallization, subsequent to cooling (still maintaining scalar decoupling), the resonant line widths of linear and branched polyethylenes increase by factors of from ten to fifty when measured at ambient temperature at 67.9 MHz. A set of typical results for linear and branched polyethylenes are given in Table 5. Crystallization thus has a major

TABLE 5. Carbon-13 NMR line widths (in Hz) for polyethylenes at 67.9 MHz and 30°C (7)

Polymer	Branching ^(a)	$(1-\lambda)_d$ ^(b)	Morphology ^(c)	Line Width
BPE-8	7	0.53	<u>b/c</u> spherulites	600 ± 30
BPE-9	12.8	0.47	<u>b</u> spherulites	550 ± 30
BPE-1	17.0	0.48	<u>b/c</u> spherulites	525 ± 25
BPE-3	24.4	0.53	<u>c</u> spherulites/ <u>h</u> random lamellae	490 ± 25
LPE-4	----	0.74	<u>a</u> spherulites	610 ± 30
LPE-5	----	0.72	<u>a</u> spherulites	525 ± 25
LPE-6	----	0.65	<u>h</u> random lamellae	410 ± 20
LPE-7	----	0.55	<u>h</u> random lamellae	420 ± 20

(a) Total branches per 1000 C atoms

(b) Degree of crystallinity from density

(c) Morphology classified according to Ref. (9)

effect on the line width, in contrast to its influence on the other relaxation parameters. Obviously, the type segmental motions reflected in the line width, as well as certain static contributions are influenced by crystallization. Moreover, we can note from the data in the Table that the line width is governed, or modulated, primarily by the supermolecular structure rather than the level of crystallinity (7)(12). For example, at the temperature and field strength listed line widths typically range from about 400 to 600 Hz as the crystalline morphology is varied from random lamellae to well-developed spherulites. Comparison can be made at approximately the same level of crystallinity so that the effect of crystalline morphology is quite apparent. Thus, for the same level of crystallinity the broader resonant line width is associated with the more highly organized crystalline superstructure. The line widths are still found to be field dependent (7). However, the relative effect is not nearly as great as found for the pure melt. An approximate decomposition method indicates that there is a major field independent contribution to the line width of the non-crystalline component (amorphous regions). The differences in magnitude due to morphology are still maintained. This difference in line width at low decoupling power (scalar decoupling) is one of the few properties of the amorphous regions of crystalline polymers which is sensitive to morphology. Hence, it appears important to attempt to separate and identify the major contributions to the line width.

The task set forth above is not a simple one as there can be several substantial factors contributing to the line width (1)(3)(5)(6)(7). Scalar decoupled magic angle spinning (at a field strength of 75 MHz) reduces the line width to 100-150 Hz which remains invariant for spinning speeds from 1.8 kHz to at least 4.5 kHz (7). Under these conditions contributions from low frequency and near-static line broadening mechanisms such as incomplete motional narrowing due to restricted angle as well as chemical shift anisotropy are removed. Increasing the decoupling power, under static non-spinning conditions reduces the line width by several hundred Hz (17a). This procedure should remove the low frequency chain motion contribution. The morphological difference in line width is still observed. Magic angle spinning with dipolar decoupling power results in a rapid decrease in line width which becomes invariant at 100-150 Hz at a spinning rate of about 1 kHz irrespective of the morphological form. The line narrowing can be attributed to a severe reduction or removal of the contribution of the chemical shift anisotropy which appears to be the factor influenced by the crystalline morphology. We note that in the magic angle spinning experiments cited above a residual invariant line width of the order of 100-150 Hertz is found irrespective of morphological form. Cross-polarization, magic angle spinning experiments with high decoupling power yield separate crystalline and amorphous resonances for linear polyethylene (5)(6). At a field strength of 75 MHz we have found the width of the amorphous resonance to also be about 100-150 Hz at a spinning speed of 4.5 kHz (7). Thus, there appears to be a significant irreducible residual contribution to the amorphous line width in the semi-crystalline polyethylene. This contribution could be due in considerable part to chemical shift dispersion (5). Three relatively major contributions to the amorphous line width have thus been identified. Much remains for a complete quantitative analysis of the respective contributions.

TRANSITIONS

Beta transition in polyethylene

Having developed a background with respect to the carbon-13 relaxation parameters we can now direct attention to the influence of glass formation and other relaxations on these quantities for the purpose of gaining more information about the transitions themselves (8)(18)(19). Directing our attention first to the polyethylenes, it is well known that both the linear and branched polyethylenes display several different transitions which have been detected by a wide variety of physical chemical techniques. Although these are well accepted, reproducible phenomena they have been subject to a diversity of interpretations for many decades. The dynamic mechanical spectrum of the branched polyethylenes usually exhibits three loss peaks, designated alpha, beta and gamma in the order of decreasing temperature from the melting temperature (20). The alpha and gamma transitions are also generally observed in linear polyethylene. There is an occasional report of the beta transition for linear polyethylene, but this appears to be an argumentative matter (21)(22). The gamma transition is usually found in the temperature range of -150°C to -120°C; the beta transition in the region -30°C to 0°C. The alpha transition is found at a much higher temperature which has now been shown to be dependent on the crystalline morphology (23). The assignment of the glass temperature of linear polyethylene, its identification with either the beta or gamma transition, has been a matter of widespread controversy for many years (24)(25)(26).

It has been reported that high resolution carbon-13 spectra can be obtained for linear polyethylene at temperatures as low as -40°C (18). This observation, along with a deduced correlation time of about 10^{-8} s, sets an upper limit for the glass temperature. These results rule out the identification of the glass temperature with the beta transition for at least the linear polymer.

The beta transition in the branched polyethylenes, as well as ethylene copolymers, is very intense, varies with the level of crystallinity and is commonly identified with the glass temperature of this species. The same type of reasoning and experiments were applied to this type polymer as was for the linear polymer (19). Essentially two methods were employed. The temperature at which no spectra could be resolved (collapsed) was determined as well as the correlation time as a function of temperature for the backbone methylene carbon. Several types of conventional high pressure polyethylenes were studied. The low frequency dynamic mechanical spectrum was obtained for each of the polymers studied, so that in each case an unequivocal, well-defined beta transition was established independently. It was found for each sample that resolvable carbon-13 spectra could be obtained virtually coincident with or only a few degrees above the independently determined beta transition (19). From the T_1 and NOE measurements the correlation time is estimated to be approximately 10^{-9} . Both these observations indicate that also for the branched polymers the beta transition cannot be identified with the glass temperature.

Although we cannot identify the beta transition with the glass temperature, it is well defined so that it must have its origin in some other phenomena. It was suggested very early that this transition could be caused by the motion of the branch point or side group (27)(28). Comparing the motion of the two type carbons, through measurement of their respective relaxation parameters thus suggests itself. Unfortunately, for the pure hydrocarbon type branched polymers there is not sufficient separation in chemical shift between the backbone methylene and the branch point methine carbons to carry out the appropriate experiments. The resonances are too close to one another so that overlap occurs as the beta transition is approached. However, for a copolymer, such as ethylene-vinyl acetate, the separation is sufficient so that the necessary experiments can be carried out. Hence, it has been possible to determine the T_1 's and NOE's, and thus the correlation times, for both carbons as a function of temperature over the range of interest (29).

Ethylene-vinyl acetate copolymers also display well-defined beta transitions so that the necessary comparisons can be made. It is found, as in the case of the hydrocarbon branched polymers, that a resolvable carbon-13 spectrum for the methylene backbone carbon can be obtained at, or within a few degrees of the independently determined beta transition (29). However, the resonance associated with the methine carbon is lost about twenty degrees above this transition temperature. Corresponding differences are found in the magnitude and temperature dependence of the T_1 's and NOE's and thus in the correlation times (29). The motion of the methine carbon is significantly retarded as the beta transition is approached and very large correlation times are extrapolated into the beta transition region. Thus there are major differences in the motion of the two types of carbons. The loss of spectra and correlation time measurements give support to the premise that branch point, and possibly the side group are involved in the beta transition.

Glass temperature

To explore the use of these methods to investigate glass formation and the glass temperature a set of eight completely amorphous homopolymers and copolymers, whose glass temperatures are well established and non-controversial, have been studied (29). The shapes of the correlation time (determined from T_1 and NOE) temperature curves are similar to one another. The curves are, however, displaced along the temperature axis from one another. The relative shifting on this axis is qualitatively dependent on the glass temperature. The temperatures at which spectra can no longer be resolved (collapse of spectra) correspond to a correlation time of about 10^{-7} s. The order of magnitude of this correlation time is expected in terms of simple line width consideration.

Except for polyisobutylene, the ratio of the temperature at which the spectra collapse to the glass temperature is in the range 1.2 - 1.3. For polyisobutylene this ratio is 1.4, which is an experimentally significant difference. Because of the apparent constancy of this ratio, the temperature for spectral loss has been identified with an amorphous transition T_{11} (30). The existence of such a transition has, however, been seriously questioned on completely other grounds (31)(32). If such a transition does in fact exist, it must merely correspond to a correlation time of 10^{-7} s.

There is, on the other hand, a natural explanation to the ratio described above. The correlation time-temperature data are found to obey the Williams, Landel, Ferry (WLF) (33) relation, with the reference temperature in this expression being identified with the glass temperature. Moreover, as is seen in Table 6, when a direct comparison can be made, the constants c_1 and c_2 determined from the carbon-13 nmr studies are in very good agreement with the corresponding quantities determined by other methods. Not only is the agreement very good, but for those polymers where data is not available so that a comparison cannot be made, very reasonable values are obtained for the parameters c_1 and c_2 . Polyisobutylene and cis-polyisoprene have virtually identical glass temperatures, but it has been known for a long time, from dynamic mechanical measurement, that there is a large difference in their respective c_2 values (34). The same results are independently obtained from the carbon-13 measurements. They explain of course the different correlation-time temperature relations for the two

TABLE 6. Comparison of WLF constants from carbon-13 nmr and other methods (29)

Polymer	NMR		Other (34)	
	c ₁	c ₂	c ₁	c ₂
Ethylene-propylene copolymer(a)	15.4	67.7	13.1	40.7
cis-polyisoprene	14.9	68.7	16.8	53.6
poly isobutylene	14.1	91.5	16.6	104.4
atactic polypropylene	15.2	60.7		
ethylene-butene copolymer(b)	13.5	40.6		
poly vinyl acetate	15.1	62.0	15.6	46.8
poly isopropyl acrylate	12.2	53.6		
cis polybutadiene	16.2	64.6		

(a) 63 mole % propylene
(b) 26 mole % butene

polymers and that the spectra collapse at different temperatures (12)(29). Therefore, these temperatures have different ratios to the glass temperature. The adherence of the nmr data to the WLF relation thus explains, in a very natural way, the temperature at which correlation times reach 10^{-7} s, the collapse of the spectra and the similar ratio of this temperature to T_g for all but polyisobutylene. Thus, if the transition T_{11} is defined by this ratio, its existence is just a consequence of the William, Landel, Ferry relation.

It is of course tempting to apply these methods to determine the controversial glass temperature, particularly those among the semi-crystalline polymers. Correlation time-temperature data are available over an extended range for polyethylene and polyethylene oxide (3)(29). Considering the possibility and complexity of a changing amorphous structure it is surprising that the results for these two polymers can be fitted by the WLF relation (33). There is, however, an uncertainty of about ± 10 to 15°C , from these data, as to the assignment of T_g when it is identified with the reference temperature. Hence, at present controversial details with respect to the glass temperature of these polymers cannot be resolved by the available data. Upper limits (18) and the temperature range of concern can, however, be established (29) so that some progress is made.

CONCLUSION

The scalar decoupled relaxation parameters are seen to be useful quantities in describing the motion and structure of the non-crystalline regions of semi-crystalline polymers. They are particularly helpful in understanding secondary transitions; behave classically with regard to glass formation of completely amorphous polymers and have the potential of leading to a better understanding of the assignment of the glass temperature in semi-crystalline polymers. Complementary studies involving dipolar decoupling and magic angle spinning should help resolve some of the outstanding problems with respect to these transitions.

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