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## Dielectric Relaxation of Oxide Polymers in Dilute Solution\*

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**ABSTRACT:** Dielectric relaxation measurements were made on dilute solutions of poly(propylene oxides) in benzene over a wide frequency range from 10 MHz to 10 GHz using time-domain reflectometry. Two relaxation processes were found. The lower frequency process, depending strongly on the molecular weight, is explained completely by the normal mode theory of Rouse and Zimm. Another process, independent of molecular weight, is caused by an elementary process in the backbone motion. The magnitude of the relaxation time is explained satisfactorily by Kramers' rate constant theory at the low-friction limit, if the elementary process is assumed to be a rotational transition of a chain bond. The relaxation process observed in poly(ethylene oxide) in benzene is also explained by Kramers' theory. The effect of chemical structure of oxide polymers on the higher frequency relaxation process is discussed.

### 1. Introduction

Three kinds of dielectric relaxation processes have been found in solutions of flexible polar polymers. If a polymer has dipole components parallel to its chain contour, a rotational diffusion of the polymer molecule gives rise to a relaxation process depending on molecular weight in a relatively low frequency region.<sup>1</sup> The relaxation time is explained quite satisfactorily by the normal mode theory of Rouse and Zimm.<sup>2,3</sup> The theory predicts relaxation time as

$$\tau_{\text{rot}} = A_1 M[\eta]\eta_0/RT \quad (1)$$

where  $M$  is the molecular weight,  $[\eta]$  the intrinsic viscosity,  $\eta_0$  the solvent viscosity,  $R$  the gas constant, and  $T$  the absolute temperature. The factor  $A_1$  takes a value of 1.21 for the free-draining case and 0.85 for the nondraining case. Poly( $\epsilon$ -caprolactone) (PCL) and poly(olefin sulfones) in solution exhibit this relaxation process.<sup>4-6</sup>

Generally, polar polymers have dipole components perpendicular to the chain contour and show a relaxation process independent of molecular weight which is observed in a relatively high frequency region.<sup>7-9</sup> Chain motions associated with conformational transitions in the chain backbone give rise to this relaxation. Recent study of methyl methacrylate-methyl acrylate copolymers in dilute solution has indicated that the elementary process in the chain motion is essentially a bond rotation which occurs independently between isomeric transition states.<sup>10</sup>

Poly(*p*-chlorostyrene) is a typical polymer having a dipole component of this type. The relaxation peak was found at about 30 MHz in solution.<sup>7-9</sup> The relaxation time is expressed experimentally by<sup>7</sup>

$$\tau_{\text{back}} = A_2 \eta_0 \exp(\Delta H_A/RT) \quad (2)$$

This expression is explained quite satisfactorily by Kramers' rate constant theory at the high-friction limit.<sup>11,12</sup> The value of  $\Delta H_A$  represents the potential barrier height for bond rotation. If correlated motions are assumed to exist among several neighboring bonds, the magnitude of the factor  $A_2$  is explained by Kramers' theory.<sup>7</sup>

If the relaxation peak is found at a frequency lower than 100 MHz, the same argument can hold well for other polar polymers such as vinyl polymers<sup>7,8</sup> and poly(alkyl methacrylates)<sup>13</sup> in dilute solution.

Recently, a relaxation caused by internal rotations of side groups has been found in poly(methyl vinyl ketone) in benzene.<sup>14</sup> Rotation of acetyl side groups gives a relaxation peak at 1 GHz. Relaxation of this kind in the solid state is observed in a number of polymers. This result indicates that relaxation caused by side-group rotation exists even in a dilute polymer solution.

If a polymer contains oxygen atoms in the chain backbone, as in the polyethers, a dielectric relaxation peak occurs at a very high frequency. Poly(ethylene oxide) (PEO) exhibits a peak at about 10 GHz in benzene,<sup>15</sup> and PCL has one at 2 GHz in dioxane.<sup>4,16</sup> Poly(styrene oxide) (PSO) shows a peak at 450 MHz in benzene, which is about 5 times higher than that of polystyrene.<sup>14</sup>

Most likely, the backbone motions in these polymers also cause the relaxation observed. Therefore, it is thought to be quite important in interpreting chain dynamics to examine whether Kramers' rate constant at the high-friction limit can or cannot be applied to the relaxation times of these polymers as well as of vinyl polymers and to determine why the relaxation time is very small in comparison with other polar polymers.

In this work poly(propylene oxides) with different molecular weights were used as the polymer having oxygen atoms in the chain backbone, and dielectric relaxation

\* This paper is dedicated, with great pleasure and appreciation, to Professor Walter H. Stockmayer on the occasion of his 70th birthday celebration.

# Dialectric Relaxation Of Dilute Polystyrene Latices

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web als je je terug in een relatie wilt haasten is de kans groot dat je niets geleerd hebt en dat je niets nieuws zult ervaren als je je ex pijn hebt gedaan zal hij ook tijd nodig hebben om het vertrouwen te herstellen doe het rustig aan en ga niet te snel voor iets

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web sep 27 2018 denk je erover om weer een relatie met je ex te beginnen hieronder een aantal vragen die je jezelf kunt stellen en bespreken met je ex voor je weer een relatie met hem of haar instapt

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web denk goed na over wat jij gedaan hebt dat bijdroeg aan het mislukken van de relatie en begin met een schone lei door je excuses aan te bieden aan je ex neem de volledige verantwoording voor wat je verkeerd hebt gedaan zonder je ex ergens de schuld van te geven smoesjes te verzinnen of een excuus terug te verwachten of vergeving

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web stop met het proberen terug te krijgen van je ex als de relatie ongezond was of als je werd mishandeld het voelt misschien tijdelijk eenzaam of zelfs saai zonder die stormachtige relatie maar probeer dat gevoel uit te zitten in plaats van weer terug naar je ex te willen

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web de problemen zullen in de eerste fase van jullie hereniging niet voelbaar zijn maar zeker wel weer naar boven komen naar gelang de tweede relatie duurt er is maar weinig kans dat de relatie perfect zal zijn helaas maar waar veel mensen die weer terug bij elkaar komen gaan meestal weer uit elkaar en zullen diezelfde pijn weer moeten doorstaan

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web nov 29 2018 als je overweegt om de relatie met je ex terug een kans te geven dan is het verstandig om allebei terug naar de basis te gaan die basis begint met een goed en opbouwend gesprek uit dat gesprek ga je een dialoog aan met elkaar om te polsen of de relatie wel of geen slaagkansen heeft

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web nov 23 2022 1 geef je ex tijd en ruimte blijf uit de buurt en laat hem of haar met rust bel niet ga niet langs hoe moeilijk dat ook is als jullie ver uit elkaars buurt zijn kunnen jullie beide voelen hoe het is om apart te leven en voelen hoeveel de ander jou ook mist en dan maar hopen dat dat het geval is

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web may 17 2021 dus je wil weten hoe je je ex terug kan winnen je hebt relaties gehad waarvan je wist dat de andere persoon niet goed voor je was maar eens in de zoveel tijd komt het ook weleens voor dat je bij iemand weggaat en dat je erachter komt dat je een grote fout hebt gemaakt

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web methode 1 denk na over de relatie 1 geef jezelf wat ruimte als je altijd maar in de buurt van je voormalige vlam bent kun je niet goed afstand nemen om te bekijken wat er nu eigenlijk fout ging hoewel je hem niet hoeft te negeren moet je hem niet bellen spreken en zelfs geen contact hebben via facebook

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web 1 krijg je leven weer op de rit je hebt een tijd een relatie gehad en misschien heeft je vriendin het wel uitgemaakt je voelt je op dit moment erg verdrietig en alleen maar focus je op de dingen die je aan jezelf kunt veranderen voordat je

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web je krijgt het gevoel dat de relatie niet meer te redden is maar dat is niet waar het is namelijk mogelijk om deze negatieve patronen te doorbreken om dit te doen is het wel heel belangrijk om jezelf kwetsbaar te maken en elkaar weer te leren begrijpen daar vertellen we in het volgende stuk meer over

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web jul 19 2022 3 min gelezen ongeacht de duur van een relatie kan het wel eens voorkomen dat er een dipje zit in de spanning tussen jullie als partners gelukkig is die spanning in je relatie er makkelijk weer in te krijgen

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