

Ultrasonic Degradation of Macromolecules in Solution. Study of Degradation Kinetics by Estimation of Free-Radical Scavenger DPPH and Solution Viscosity Measurements

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Synopsis

The kinetics of degradation of butyl rubber in two solvents, cyclohexane and toluene, was studied by two independent techniques: viscosity measurements and free-radical estimation as a function of DPPH consumed. The general shape of the rate curves in the two cases is similar, but not identical. The rate given by estimation of DPPH is faster than that obtained from solution viscosity data. This has been attributed to the inherent limitations of the two methods for the quantitative determination of the number of breaks occurring in the polymer molecules. The rate is also reduced as the viscosity of the solution medium is increased, which may be correlated with the reduction of the cavitation effect responsible for degradation. The degradation rates in two solvent media initially having the same viscosity were unequal. This may be due to different solvent-solute characteristics, which means that the viscosity and cavitation change to different extents in the two cases throughout the course of degradation. The limiting degree of polymerization $(DP)_{\infty}$ obtained after prolonged irradiation has been found to be dependent on parameters such as intensity of irradiation, solution viscosity, and initial DP of the molecules.

Introduction

Several methods¹⁻⁴ have been reported for studying the progress of ultrasonic degradation of macromolecules in solution. It has been pointed out that the number of bonds broken in the polymer molecules is an unambiguous measure of degradation,⁵ and this can be determined directly by estimating the free radicals formed with a free-radical scavenger such as α, α' -diphenyl β -picryl hydrazyl (DPPH). However, the most common and simple method has been the measurement of solution viscosity from which the molecular weight at various stages of degradation is determined. Consequently, the kinetic analysis involved primarily obtaining an average molecular weight of the degrading polymer in terms of some molecular constants. Only a few workers have compared the results obtained by employing simultaneously more than one technique. Mostafa⁶ studied ultrasonically degraded polystyrene solution using solution viscosity as

well as free-radical estimation methods, but no simple correlation was obtained between the number of breaks, as calculated via viscosities, and the consumption of DPPH; also analysis of these data by using the rate equation proposed by Jellinek and White⁷ was not fruitful. The purpose of the present paper is to present some results on ultrasonic degradation of butyl rubber in two solvents, cyclohexane and toluene, both by solution viscosity measurements and by free-radical estimation as a function of DPPH consumed. An effort has been made to explain the difference between the results obtained by the two methods.

Experimental

The irradiation source was a Mullard ultrasonic generator (type E 7562) fitted with a 500-Kc./sec. quartz transducer. The experimental procedures have been described elsewhere.^{8,9} Butyl rubber, type 402, was fractionated in the usual way and the sample under study has a molecular weight, as determined by the light-scattering method, of 1.35×10^6 . An excess ($\sim 10^{-5}$ mole) of DPPH was added to the rubber solution and after irradiation the same degraded solutions were used both for viscosity measurements and spectrophotometric estimation of DPPH. It was assumed that recombination of broken molecules was negligible, since excess DPPH present in the media has a high affinity for free radicals and thus the recombination of radicals formed by the rupture of the polymer molecule is suppressed. Further, the small quantity of DPPH present has practically no effect on the viscosity of the solutions.

The spectrophotometric measurements were carried out in a Hilger spectrophotometer in a manner similar to that described in earlier papers.^{8,9} The viscosity measurements were done with a Ubbelohde dilution viscometer thermostatted at $30 \pm 0.02^\circ\text{C}$. The flow time of solvents, cyclohexane and toluene, were 382 and 220 sec., respectively, and no kinetic energy corrections were made. The intrinsic viscosity was determined by a single point measurement by using the relation given by Naar et al.¹⁰

$$[\eta] = (1/C)\sqrt{2(\eta_{sp} - \ln \eta_{rel})} \quad (1)$$

The validity of this relation for the butyl rubber-cyclohexane and butyl rubber-toluene systems were checked by the classical three-point determination and graphical extrapolation. It was found that the values were well within the experimental error. The viscosity-average molecular weight was determined by the Mark-Houwink relation $[\eta] = KM^a$. The constants K and a were evaluated by comparing $[\eta]$ of six samples, with their molecular weights determined by the light-scattering method. The results were as follows.

In cyclohexane at 30°C .:

$$[\eta] = 9.933 \times 10^{-5} \bar{M}_v^{0.7281}$$

In toluene at 30°C .:

$$[\eta] = 8.506 \times 10^{-5} \bar{M}_v^{0.6972}$$

Since polydispersity is present in a degrading polymer solution, the viscosity-average molecular weight was changed into a number-average value by the relation:¹¹

$$\left[\frac{(\overline{DP})_\eta}{(\overline{DP})_n} \right]^a = \frac{\{\Gamma(3 + a)\}}{2^{(1 + a)}} \quad (2)$$

where Γ is the gamma function and a is the exponent in Mark-Houwink equation. The number B_t of bonds broken in time t was calculated by the relationship

$$(\overline{DP})_t = (\overline{DP})_0 n_0 / (n_0 + B_t) \quad (3)$$

where n_0 is the number of molecules present initially per gram of rubber having number-average degree of polymerization $(\overline{DP})_0$.

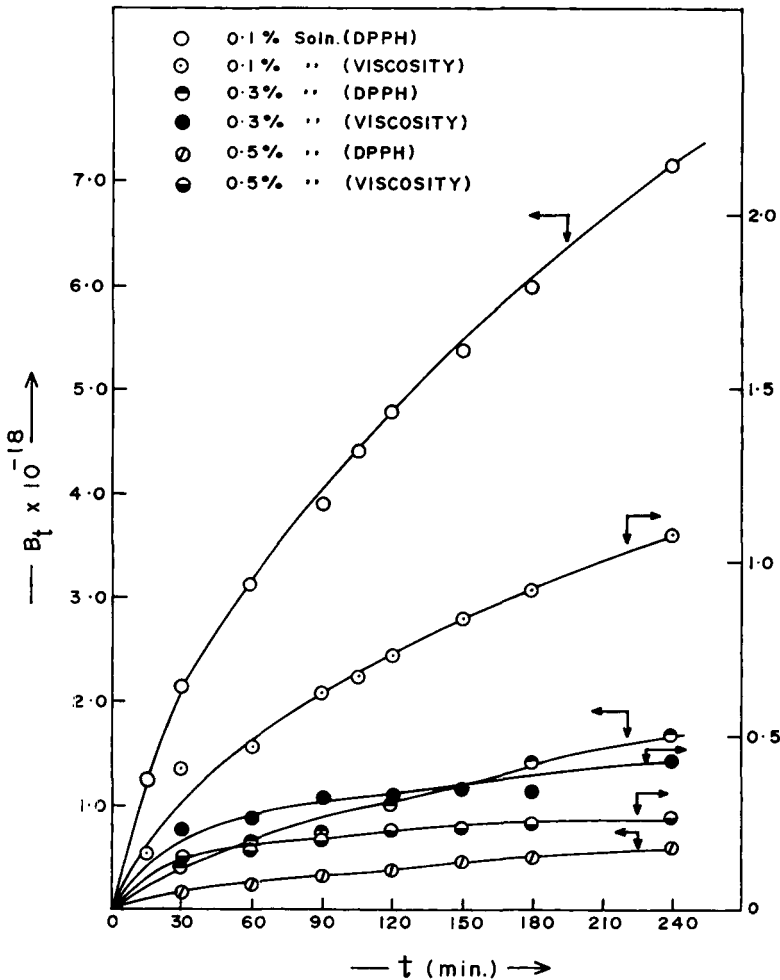


Fig. 1. Solution of butyl rubber in cyclohexane.

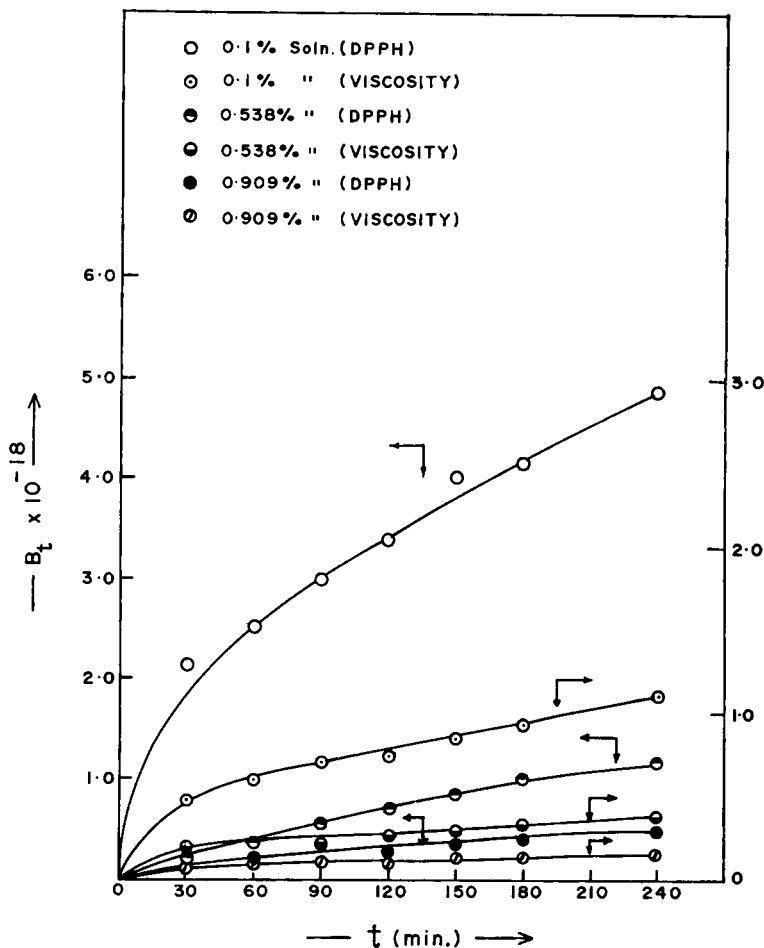


Fig. 2. Solution of butyl rubber in toluene.

Results and Discussion

The results for butyl rubber in cyclohexane and toluene are given in Figures 1 and 2. Experimentally determined values of B_t as a function of DPPH consumed and solution viscosity are plotted for different concentrations on the same graph. At the initial stages the breakdown was very rapid, but it later slowed down considerably before attaining a constant value. It is not surprising that the general shapes of the two curves are similar, since a proportional decrease of DPPH color as well as that of the solution viscosity takes place during progressive degradation.

However the main point which emerges from the above observations is that identical results are not obtained by the two techniques. Of course the techniques used for estimation are not ideal and each has its own limitation. The viscosity-average molecular weight determination requires some arbi-

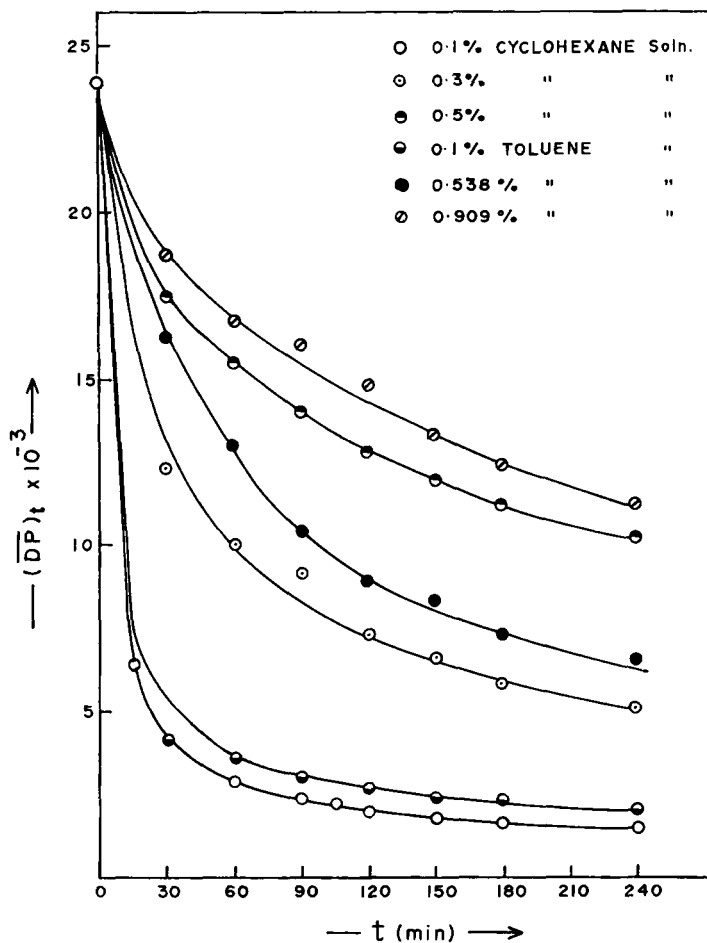
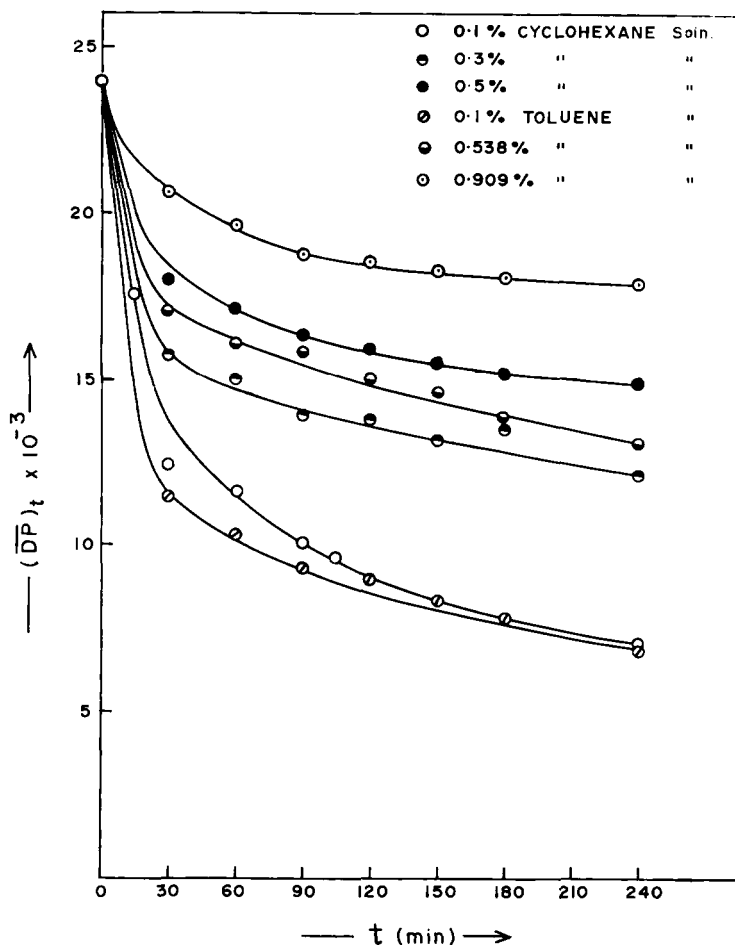


Fig. 3. $(\overline{DP})_t$, vs. t (DPPH consumption method).

rary constants to be determined from independent experiments with samples of molecular weights evaluated by the light-scattering technique. The method is therefore not absolute. On the other hand, the efficiency of DPPH as a free-radical scavenger may not be unity as we have assumed in our calculations. However, the breaks that we have estimated by these two methods may be considered as proportional to that actually taken place.

From the experimental data, suitable values for limiting degree of polymerization, P_e and kinetic rate constants, K were chosen, and the number B_t of bonds broken after irradiation time t was calculated by the rate equations developed from two different approaches: one by Jellinek and White⁷ and the other by Ovenall et al.^{12,13} Typical data are shown in Tables I and II. The data obtained by DPPH estimation showed a better fit with those calculated by Ovenall's equation, whereas much disagreement was observed,

Fig. 4. $(\overline{DP})_t$ vs. t (solution viscosity method).

especially for the more concentrated solutions, between the calculated and experimental data obtained by viscosity measurements. The details of the experimental data and degradation parameters are summarized in Table III. The rate constants obtained by free-radical estimation are several times higher (about 4–5 times for lower concentrations) than those obtained by solution viscosity measurements.

It may be seen from the data that the rate of degradation decreases as the viscosity of the solution is increased. Cavitation of the media, which is responsible for the scission of molecules, is reduced with increasing viscosity of the solution. Further, it has been observed that the butyl rubber in two different solution media initially having the same viscosity, for example, 0.1% solution in cyclohexane and 0.538% in toluene or 0.3% in the cyclohexane and 0.909% in toluene, does not degrade at the same rate. A possible explanation is that, since the viscosity changes at different rates during

TABLE I
Degradation of 0.1% Butyl Rubber in Cyclohexane
Measured by Solution Viscosity Method

Time t , min.	Viscosity- average DP $(DP)_\eta \times 10^{-4}$	Number- average DP $(\overline{DP})_n \times 10^{-4}$	Number of bonds broken/g. polymer $B_t \times 10^{-18}$	B_t calculated by Ovenall's eq. $\times 10^{-18}$	B_t calculated by Jellinek's eq. $\times 10^{-18}$
15	2.5372	1.7668	0.16	0.14	0.11
30	1.7803	1.2397	0.42	0.27	0.22
60	1.6696	1.1626	0.47	0.47	0.42
90	1.4382	1.0015	0.62	0.63	0.62
105	1.3777	0.9594	0.67	0.70	0.70
120	1.2950	0.9019	0.74	0.76	0.79
150	1.1939	0.8314	0.84	0.87	0.95
180	1.1172	0.7779	0.93	0.95	1.10
240	1.0077	0.7017	1.08	1.08	1.36

TABLE II
Degradation of 0.1% Butyl Rubber in Cyclohexane Measured
by Estimation of Free Radicals as a Function of DPPH Consumed

Time t , min.	DPPH con- sumed C , moles $\times 10^5$	Apparent no. of molecules broken/ 1000 cc. soln. $B = CN/2$ $\times 10^{-18a}$	Real no. of bonds broken/g. $B_t =$ $B \times 0.835$ $\times 10^{-18}$	B_t calculated by Ovenall's eq. $\times 10^{-18}$	B_t calculated by Jellinek's eq. $\times 10^{-18}$
15	0.50	1.5050	1.256	0.96	0.70
30	0.85	2.5585	2.136	1.79	1.39
60	1.25	3.7875	3.162	3.11	2.72
90	1.55	4.6655	3.896	4.12	3.96
105	1.67	5.0267	4.400	4.53	4.54
120	1.90	5.7190	4.775	4.85	5.11
150	2.14	6.4414	5.378	5.52	6.13
180	2.37	7.1337	5.957	6.01	7.50
240	2.85	8.5785	7.173	6.75	8.59

^a N = Avogadro's number.

the course of degradation, the cavitation intensity also varies, and the rates in the two cases would be unequal.

Figures 3 and 4 show that $(\overline{DP})_\infty$, the number-average degree of polymerization after infinite time of irradiation, obtained by extrapolating the $(\overline{DP})_t$ versus t curves to infinite time, lie in the ranges 1,300–10,000 and 6,000–18,000 for the DPPH estimation and viscosity methods, respectively. Thus, $(\overline{DP})_\infty$ as obtained through solution viscosity measurements was always 3–4 times higher than that by DPPH estimation. Also, the initial viscosity (or concentration) of the degrading solution was found to control the value of $(\overline{DP})_\infty$. The present values (1,300–1,900) for 0.1% butyl

TABLE III
Experimental Data and Degradation Parameters

Solution	Concn., g./dl.	η_0 $\times 10^{-3a}$	P_e			$(\overline{DP})_{\infty}$			$K \times 10^6, \text{min.}^{-1}$		
			DPPH	Viscosity	$(\overline{DP})_0$	DPPH	Viscosity	DPPH	Vis- cosity	Jellinek and White	
										DPPH	Vis- cosity
Butyl rubber-cyclohexane	0.1	0.4459	1,597	7,662	23,986	1,350	6,500	7.0	1.4	4.4	0.7
Butyl rubber-cyclohexane	0.3	0.4459	5,497	12,645	23,986	4,800	11,600	1.6	0.85	0.9	0.3
Butyl rubber-cyclohexane	0.5	0.4459	11,017	15,370	23,986	9,900	14,700	1.0	0.8	0.14	0.2
Butyl rubber-toluene	0.1	0.4459	2,163	7,397	23,986	1,900	6,300	5.5	1.5	3.2	0.8
Butyl rubber-toluene	0.538	0.4459	7,150	13,875	23,986	5,500	12,800	1.2	0.7	0.65	0.3
Butyl rubber-toluene	0.909	0.4459	12,211	17,949	23,986	10,100	17,700	0.68	—	0.3	—
Butyl rubber-cyclohexane ^b	0.1	0.3628	2,248		28,482	1,750		4.8		3.2	
Butyl rubber-cyclohexane ^b	0.1	1.038	2,901		10,305	2,700		2.5		1.55	
Natural rubber-cyclohexane ^c	0.075	0.2069	1,017		42,390	950		8.1		6.5	
Natural rubber-toluene ^c	0.075	0.2069	2,520		42,390	2,200		2.5		2.0	
Polystyrene-benzene ^d	0.208		1,780		3,650	1,330		5.3			
Polystyrene-toluene ^d	0.185		1,740		3,650	1,310		13.3			
Poly(methyl methacrylate)-benzene ^d	0.199		2,800		3,900	2,100		15.0			

^a Butyl rubber solutions in 22-cc. portions were used throughout.

^b Data of Chandra et al.⁹

^c Data from Chandra et al.⁸

^d Data from Allen et al.⁵

rubber compare well with those reported earlier (1,000–2,200) for 0.075% natural rubber solution.

It is interesting to note that Allen et al.⁵ obtained for about 0.2% solution of polystyrene in benzene and toluene (Table III), a $(\overline{DP})_{\infty}$ around 1,300 and for poly(methyl methacrylate) in benzene a value of about 2,100, which values are of the same order as our results, even though the $(\overline{DP})_0$ of their samples was about six times lower. Considering our earlier results⁹ that $(\overline{DP})_{\infty}$ seems to depend on the initial DP of the polymer used, the comparatively lower values of Allen et al. may be attributed to either the characteristics of the solvent-solute system in relation to cavitation formation or to the higher irradiation intensity used by them.

It may be concluded that all reported values of $(\overline{DP})_{\infty}$ are appreciably influenced by parameters such as viscosity of the solution, intensity of the irradiation, and $(DP)_0$ of the degrading molecules.

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Résumé

La cinétique de dégradation du caoutchouc butylique dans deux solvants, savoir le cyclohexane et le toluène, a été étudiée en employant deux techniques indépendantes: des mesures de viscosité et l'estimation de la concentration en radicaux libres en fonction de la quantité de DPPH consommé. L'allure générale des courbes de vitesses dans ces deux cas est semblable, mais non identique. La vitesse donnée par estimation du DPPH est plus rapide que celle obtenue au départ de données viscosimétriques en solution. Ceci a été attribué aux limitations inhérentes aux deux méthodes pour la détermination quantitative du nombre de cassures qui se passent au sein de molécules polymériques. La vitesse est aussi réduite lorsque la viscosité moyenne de la solution est accrue, ce qui peut être relié à la réduction de l'effet de cavitation responsable pour la dégradation. Les vitesses de dégradation dans les deux solvants considérés ayant initialement la même viscosité, sont trouvées inégales entre elles. Ceci peut être dû à des caractéristiques solvant-solute différentes par laquelle la viscosité et le phénomène de cavitation changent de façon différente dans les deux cas tout au cours de la dégradation. Le degré de polymérisation limite $(DP)_{\infty}$ obtenu après irradiation prolongée a été trouvé dépendant des

paramètres tels que l'intensité de l'irradiation, la viscosité de la solution et le poids moléculaire initial des molécules.

Zusammenfassung

Die Kinetik des Abbaues von Butylkautschuk in zwei Lösungsmitteln (Cyclohexan und Toluol) wurde nach zwei unabhängigen Verfahren untersucht: Viskositätsmessungen und Bestimmung der freien Radikale durch den Verbrauch von DPPH. Der allgemeine Verlauf der Geschwindigkeitskurven ist in beiden Fällen ähnlich, aber nicht identisch. Die nach der DPPH-Methode erhaltene Geschwindigkeit ist grösser als die aus den Lösungsviskositätsresultaten bestimmte. Dies wurde auf die spezifischen Begrenzungen der beiden Methoden bei der quantitativen Bestimmung der Anzahl der in den Polymermolekülen auftretenden Kettensprengungen zurückgeführt. Weiters wird die Geschwindigkeit durch die Zunahme der Viskosität der Lösung herabgesetzt, was in Korrelation zur Herabsetzung des für Abbau verantwortlichen Kavitationseffekt gesetzt werden kann. Die Abbaugeschwindigkeit in den beiden Lösungen mit gleicher Anfangsviskosität war verschieden. Dies kann auf eine verschiedene Charakteristik Lösungsmittel-Gelöstes zurückzuführen sein, wodurch sich in den beiden Fällen die Viskosität und das Kavitationsphänomen im Verlauf des Abbaus in verschiedenem Ausmass ändern. Der nach längerer Bestrahlung erhaltene Grenzpolymerisationsgrad $(\overline{DP})_{\infty}$ war von Parametern, wie Strahlungsintensität, Lösungsviskosität und Anfangs-DP der Moleküle abhängig.

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