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Q and e Values of Telogens

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ABSTRACT

By using a linear least-squares technique, the Q and e values of a number of telogens have been determined.

Ham [1, 2] and Fuhrman and Mesrobian [3] have attempted to assign reactivity parameters to free radically active telogens. The former approach was part of a new general reactivity scheme which could supplant but not surpass the Q and e scheme [4]. The latter study successfully assigned Q and e values to a single telogen, carbon tetrabromide.

By using the previously reported linear least-squares technique for the determination of Q and e values for vinyl monomers [5], Q and e values were determined for a group of telogens. In this case the reciprocal of the chain transfer constant, $1/C_s$, replaced r_1 :

$$\left\{ \left[\ln Q_1 / (1/C_s) \right] - e_1^2 \right\} = -e_1 e_2 + \ln Q_2$$

The Q_1 and e_1 values for the vinyl monomers are from a completely revised and expanded listing based on Young's latest published

TABLE 1. Q and e Values of Telogens

Telogen	Polymerization at 60° C				Polymerization at 80° C			
	Q × 10 ⁴	e	r ^a	No. b	Q × 10 ⁴	e	r ^a	No. b
Acetone	0.11	+0.38	0.73	(4)	0.30	+0.63	0.82	(4)
Benzene	0.05	-1.41	0.95	(7)	0.07	-0.70	0.51	(8)
Chloro-	0.03	-1.00	0.98	(5)	0.14	-0.71	0.75	(7)
Ethyl-	1.01	-1.07	0.97	(6)	1.03	-0.75	0.99	(5)
Methyl-	0.21	-0.56	0.66	(5)	0.35	-0.42	0.51	(7)
Benzoyl Peroxide	45.0	-1.41	0.93	(4)				
Butanol	0.53	- .57	0.61	(6)				
Butanone	0.83	+ .54	0.60	(4)	1.30	+1.18	0.84	(6)
Cyclohexane	0.08	- .98	0.82	(5)	0.11	-0.91	0.64	(4)
1,2-Dichloroethane	0.19	+ .04	0.19	(3)	0.61	+0.31	0.31	(4)
Ethyl acetate	0.08	-1.03	0.96	(6)				
Mercaptan, alkyl	15000.	+2.31	0.99	(11)				
Mercaptoacetate, alkyl	15100.	+3.26	0.99	(4)				
Methane								
Dichloro-	0.09	- .70	0.82	(4)				
Nitro-	3.36	+1.51	0.90	(4)				

Tetrabromo-	3300.	+1.51	0.99	(5)			
Tetrachloro-	3.61	+3.62	0.98	(6)	4.09	+3.48	0.97 (7)
Trichloro-	0.35	-0.31	0.82	(3)	0.54	-0.14	0.48 (6)
Methanol	0.13	-0.87	0.63	(7)			
Triethylamine	27.0	-2.12	0.98	(6)			

^a_r = correlation coefficient.

^bNo. = number of chain-transfer constant citations used in the evaluation.

tabulation of reactivity ratios [6]. The chain transfer constants are from another tabulation by Young [6].

Since chain transfer activity is usually a function of temperature, the telogen Q and e values were determined for both 60 and 80°C when sufficient data were available. The results are shown in Table 1.

As expected, the Q values of the telogens all increased to some degree at the higher temperature. Also, for nine out of ten telogens, the e values were more positive at 80°C. Butanone, ethyl acetate, and ethylbenzene have e values similar to those of the corresponding unsaturated vinyl monomers. (The Q and e values for 1,2-dichloroethylene could not be determined with the available reactivity ratios.)

It is unfortunate that insufficient data exist to evaluate the chain-transfer behavior of other important solvents such as dimethylformamide, dimethyl sulfoxide, and the cyclic ethers. But it is hoped that this listing of Q and e values will prove useful to the synthetic polymer chemist.

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