Question 1.
In order to calculate the molecular weight of a mixture of polystyrene after sonication, the following equation can be applied

$$\frac{1}{M_{n,t}} = \frac{1}{M_{n,0}} + k^{`}t$$

and

$$k^{`} = \frac{k}{M_o}$$

In which $M_{n,t}$ is the number average molecular weight after t min of sonication, $M_{n,0}$ is the initial number average molecular weight, M_o is the molecular weight of the monomer unit and k is the degradation rate (x 10^{-6} min^{-1})

(a) Consider a mixture of polystyrene ($C_6H_5CH{=}CH_2$) with an average number molecular weight of 500kD and a rate constant of 0.22, what is the number average molecular weight of the mixture after 300 min of sonication?

(b) Taking the same mixture as in the previous question, how long would you need to sonicate this mixture to reduce the molecular weight to half of the original?

(c) Degradation of a polymer under ultrasonication only occurs if the molecular weight of the polymer is high enough, as the length of the polymer plays a role in the arising forces. As a consequence, degradation does not continue indefinitely, but only until the polymer chains have reached a limiting molecular weight. For polystyrene in toluene this limited is represented by:

$$M_{n,lim} = 41\,800 - 90.8\ x\ I\ (W\ cm^{-2})$$

Calculate the number average molecular weight of the polystyrene mixture after sonicating until reaching the point at which no more degradation occurs, for the following intensities: 50, 100, and 200 W cm^{-2}

ANSWER:

(a)

$$k^{`} = \frac{0.22\ x\ 10^{-6}}{104} = 2.12\ x\ 10^{-9}$$

$$M_{n,t} = \frac{1}{\frac{1}{M_{n,0}} + k^{`}t} = \frac{1}{\frac{1}{500000} + 2.12\ x\ 10^{-9}\ x\ 300} = 379562$$

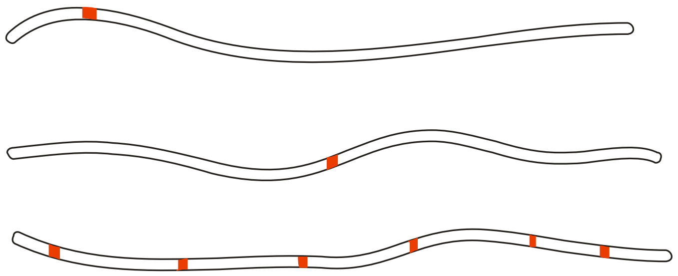
(b) $$t = \frac{\frac{1}{M_{n,t}} - \frac{1}{M_{n,0}}}{k^{`}} = \frac{\frac{1}{250000} - \frac{1}{500000}}{2.12\ x\ 10^{-9}} = 945\ \text{min}$$

(c)

$M_{n,lim}$	I
37260	50
32720	100
23640	200

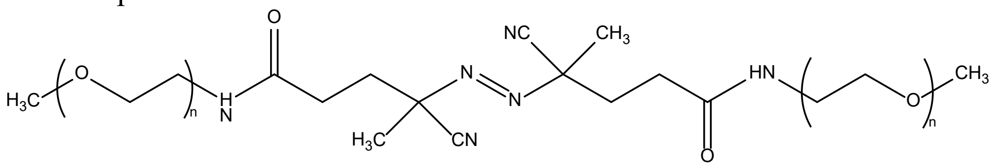
Question 2.

The following polymers all have been synthesized containing one or more breakable mechanophores (in red) at different positions along the polymer chain. Describe a method to test whether these mechanophores are active and described the results that would indicate scission of the polymer chain at the position of the mechanophores.



ANSWER: Monitoring the polymer molecular weight with GPC allows to probe if chain scission occurs. The first two polymers undergo one scission event, the last one can undergo up to 6. Other techniques such as solution viscometry or rheology may also provide sight since viscosity is also molecular weight dependent, but the changes may be less pronounced and it may be hard, in particular in case of the last polymer to conclude anything about the number of scission events. The use of ^{13}C labels and NMR or spin traps and ESR (see https://www.sciencedirect.com/science/article/pii/0009261480852304) can provide way to monitor the chain end groups that are formed upon chain scission.

Question 3.
A group of scientists has synthesized the polymer shown below, which has a build-in mechanophore.



(a) To test whether their theory works, they subject a solution containing the polymer to ultrasonication and analyze the results. Using the table (last page) of bond dissociation energies, indicate where the molecule is most likely to break.

(b) The polymer is synthesized with an n of 450. Draw the molecular weight distribution of the polymer i) before sonication, ii) after sonication, and iii) half-way the sonication procedure.

Lowry, T. H.; Richardson, K. S. "*Mechanism and Theory in Organic Chemistry*"

Harper & Row, 1987 pp 161-162

FOR VARIOUS TYPES OF BONDS

Bond Dissociation Energies[a,b]—Single Bonds: Diatomic Molecules

Bond	Energy	Bond	Energy	Bond	Energy
H—H	[436.0]	F—Cl	[255]	H—F	[568]
D—D	[444.5]	F—Br	[251]	H—Cl	[431]
F—F	[159]	F—I	[243]	H—Br	[366]
Cl—Cl	[243]	Cl—Br	[218]	H—I	[298]
Br—Br	[192]	Cl—I	[209]		
I—I	[151]				

Polyatomic Molecules

Bond	Energy
CH_3CH_2—$CHCH_2$	[372]
CH_3CH_2—C_6H_5	[377]
CH_2CH—$CHCH_2$	[418]
HCC—CCH	[628]
C_6H_5—C_6H_5	[418]
CH_2CH—C_6H_5	[414]
CH_3—$COCH_3$	[343]
CH_3CH_2—$COCH_3$	[331]
CH_3—CN	[510]
CH_2CH—$COCH_3$	[372]
CH_2CH—CN	[536]
CH_3CO—$COCH_3$	[347]
CH_3CNHC—$NNCHCNCH_3$	[290]
CF_3—CF_3	[406]
H—OH	[498]
H—O_2H	[377]
H—SH	[377]
H—OCH_3	[427]
H—OC_6H_5	[356]
H—O_2CCH_3	[469]
HO—CH_3	[383]
HO—CH_2CH_3	[383]
HO—C_6H_5	[431]
HO—$COCH_3$	[456]
CH_3O—CH_3	[335]
CH_3O—CH_2CH_3	[335]
CH_3O—$CHCH_2$	[366]
CH_3O—C_6H_5	[381]
CH_3O—$COCH_3$	[406]
HO—OH	[213]
HO—Br	[238]
CH_3O—OCH_3	[151]
H_2N—H	[431]
H_2N—CH_3	[331]

[a] From Gordon, A. J.; Ford, R. A. "The Chemists Companion"; Wiley: New York, 1972. Reprinted by permission of John Wiley & Sons. Copyright 1972 John Wiley & Sons, Inc.

Numbers in brackets are values in kJ mol^{-1}.

ANSWER: n=450 equals a total MW of 40kDa (394.48 mwt + 44.05 x 2 x 450). Sonication will lead to 2 x 20 kDa fragments, before sonication there are only polymer chains of 40kDa, after sonication there are only 20kDa fragments (twice the amount of initial chains). After half of the chains have broken there is a half the initial amount of 40kDa chains and the amount of 20kDa fragments equals the initial amount of polymer chains. i) blue, ii) red, iii) green.