PS #6

51.

In example 4.1, at some indicated time, the polymer was terminated and analyzed for molecular weight. For ideal living anionic polymerization, the conversion p should have a relationship with time as

$$p = 1 - \exp(-k_p [I]_0 t) \quad 1$$

And p is derived indirectly from N_n assuming the following relation is accurate:

$$p = N_n [I]_0 / [M]_0 \quad 2$$

In the real system, due to some non-ideality, equation 2 might be not correct. If the relation between conversion and time was the object, the conversion should be calculated directly based on the actual yield of polymers.

52.

There are four requirements for living polymerization, which lead to Poisson distribution:

1. A living polymerization proceeds in the absence of transfer and termination reactions.
2. All active chain ends must be equally likely to react with a monomer throughout the polymerization (equal reactivity and good mixing of reagents at all times).
3. The rate of initiation needs to be much more rapid than the rate of propagation.
4. Propagation must be essentially irreversible

N_n	PDI(Exp.)	PDI(Poisson)	PDI(p)/PDI(e)
36.3	1.06	1.026	0.968
198	1.02	1.005	0.985
324	1.02	1.003	0.983
413	1.01	1.002	0.992
479	1.008	1.002	0.994
528	1.006	1.002	0.996
593	1.005	1.002	0.997

$$\text{*PDI (Poisson)} = \frac{N_W}{N_N} = 1 + \frac{\bar{v}}{(1+\bar{v})^2}$$

If condition 1 is not satisfied, for example, a living chain transfers to another polymer chain, there will be a relatively big increase in PDI.

If condition 2 is not satisfied, PDI will slightly increase for further polymerization

If condition 3 is not satisfied, PDI difference will be smaller as the reaction goes on, because the slow initiation effect will be reduced as the polymer becomes bigger.

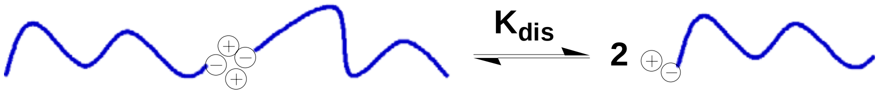
If condition 4 is not satisfied, which means that adding a monomer is reversible, the PDI will increase as the polymerization goes on, and finally approaches 2.

Based on the results in example 4.1, condition 3 is most probably not satisfied.

53.

The key factor that comes into play in non-polar solvents is ion-pairing or clustering of the living ends. Ionic species tend to be sparingly soluble in hydrocarbons, as the dielectric constant of the medium is too low. The rate of polymerization is therefore first order in monomer concentration and has a (1/n) fractional dependence on initiator concentration, n is the aggregation number.

For living polymerization of styrene in cyclohexane, it is known that rate is in 0.5 order to initiators, so clusters with n = 2 are the main species.



$$k_{app} = k_p (K_{dis}/2)^{1/2}.$$

$$k_p = 1000 \text{ mol/L/s and } k_{app} = 1 \text{ mol/L/s}$$

$$K_{dis} = 2 * 10^{-6}$$

54.

A living polymerization is defined as a chain growth process without termination or transfer reactions. For living polymerization, M_n increase with the conversion. However, the fact that M_n increases with the conversion is not sufficient for living polymerization.

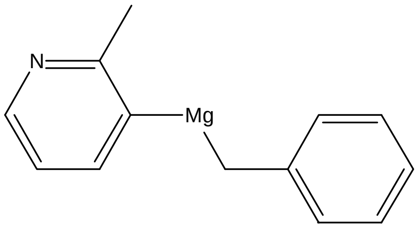
For example, in a system containing 5 initiators and 100 monomers

Initiator	M(P=25%)	M(P=60%)	M(P=80%)	M(P=100%)
1	5	12*	12*	12*
2	5	12	17*	17*
3	5	12	17*	17*
4	5	12	17	27
5	5	12	17	27
M_n	**5**	**12**	**16**	**20**

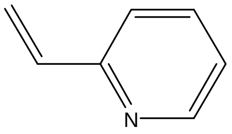
*dead polymers

Generally, even though termination is present in the system, M_n is still linear with conversion. Mn increases linearly with the conversion if the number of chains is fixed. But, if the number of chains decreases linearly with conversion by termination, Mn will still be linear with conversion. Or, if transfer reactions do not change the number of living reaction centers, Mn will still be linear with the conversion.

55.



benzyl picolyl magnesium



2-vinyl pyridine (M=105)

[I](mmol/L)	[M]$_0$(mmol/L)	M(cal) (kg/mol)	M(exp) (kg/mol)	M(cal)/M(exp)
0.48	82	17.9	20	0.895
0.37	85	24.1	25	0.964
0.17	71	43.9	46	0.954
0.48	71	15.5	17	0.912
0.58	73	13.2	14	0.943
0.15	150	105	115	0.913

Calculate the expected Mn assuming complete conversion and 100% initiator efficiency. Experimental data corresponds with calculated data fairly well if considering some inefficiency in the initiation step. (< 100% efficiency in the initiator is quite common, for example due to degradation of the rather reactive initiators on storage).