SOLUTIONS MANUAL FOR

Introduction to Polymer Science and Chemistry: A Problem-Solving Approach, Second Edition

by

Manas Chanda

CRC Press
Taylor & Francis Group

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Preface

This solutions manual for *Introduction to Polymer Science and Chemistry: A Problem Solving Approach, Second Edition*, henceforth referred to simply as 'polymer text', is prepared mainly for those professors, instructors, and teaching assistants who are using the polymer text as a textbook. Most of the exercise problems being of numerical type, these are fully worked out in the manual making use of the theoreticl equations and/or concepts derived in the polymer text. Non-numerical questions which are directly related to the polymer text in some way or other are answered briefly in the context of the discussion given in the polymer text, while a few questions which are not directly related to the polymer text are answered in greater detail.

The manual has twelve chapters containing 277 solved problems. Ten of the chapters relate to conventional topics of polymer science and chemistry, ranging from molecular characteristics and chain structures, transitional properties, and solid state and solution behavior to classical methods of polymerization, which, in turn, range from condensation, free-radical, ionic, and coordination to ring-opening polymerization. The remaining two chapters relate to two recent topics that currently dominate the field of polymer chemistry, namely, living/controlled radical polymerization and application of click chemistry for polymer synthesis. As such, the exercise problems for these two chapters are mostly drawn from current literature. The number of corresponding references being significantly large, these are listed separately at the end of the respective chapter. For other chapters, however, the relevant references are cited within the text at the same place where they occur.

Deviating from the normal practice of having only the answers in a solutions manual, in the present case each answer is preceded by the question reproduced from the textbook. This is done keeping in view the fact that the polymer text was specially designed with emphasis on problem solving, and accordingly the end-of-chapter problems were carefully chosen and graded to reflect the whole range of topics covered in each chapter. Thus with both problems and their worked out solutions given in the same place, this solutions manual may also serve as a book of solved problems in polymer science and chemistry.

Though this solutions manual can be used independently as a book featuring solved problems of polymer science and chemistry, which are presented in a comprehensive and systematic manner, it will indeed be an advantage to have the polymer text alongside, since all equations and most of the concepts made use of in the solutions are derived and explained in the polymer text. In order to formalize this interlink, all figures, tables, and equations that arise in the course of solving the exercise problems have been numbered with prefix 'E', while those numbers without the prefix 'E' invariably refer to the polymer text.

As the exercises in the polymer text are the products of my many years of teaching the subject both at the Indian Institute of Science, Bangalore, and abroad during sabbaticals, the problems in the exercises were solved by many teaching assistants, working individually and under my guidance during my teaching years. I would like to thank all these people who spent considerable time to work out many of the problems as also the students my interactions with whom both inside and outside the

classroom helped shape many of the problems. While I hope the solutions presented in the manual are correct, and some problems may have more than one correct solutions, I shall appreciate being apprised if a problem is found to have been incorrectly solved.

The manual has been prepared electronically by myself. In this endeavour, I have received valuable help from Dr. P. Sunthar, who stepped in often to solve software related problems and to Ms. B. G. Girija who prepared computer graphics for all diagrams, chemical structures, and chemical formula-based equations. I am deeply indebted to both of them.

Manas Chanda

Author

Manas Chanda has been a professor and is presently an emeritus professor in the Department of Chemical Engineering, Indian Institute of Science, Bangalore, India. He also worked as a summer-term visiting professor at the University of Waterloo, Ontario, Canada with regular summer visits from 1980 to 2000. A five-time recipient of the International Scientific Exchange Award from the Natural Sciences and Engineering Research Council, Canada, Professor Chanda is the author or coauthor of more than 100 scientific papers, articles, and books, including *Plastics Technology Handbook*, 4th Edition (CRC Press, Boca Raton, Florida). His biographical sketch is listed in Marquis' *Who's Who in the World* Millennium Edition (2000) by the American Biographical Society. A Fellow of the Indian National Academy of Engineers and a member of the Indian Plastics Institute, he received B.S. (1959) and M.Sc. (1962) degrees from Calcutta University, and a Ph.D. (1966) from the Indian Institute of Science, Bangalore.

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Chapter 1

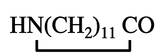
Introductory Concepts

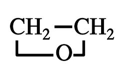
Exercises

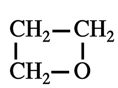
E1.1 Represent, by showing a repeating unit, the structure of the polymer which would be obtained by polymerization of the following monomers:
(a) ω-aminolauric acid; (b) lauryl lactam; (c) ethylene oxide; (d) oxacyclobutan; (e) ethylene glycol and terephthalic acid; (f) hexamethylene diamine and sebacic acid; (g) ethylene glycol and phenylene diisocyanate; (h) *m*-phenylene diamine and isophthaloyl chloride

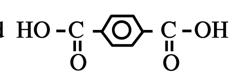
Answer:

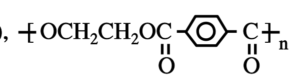
(a) Monomer: $H_2N(CH_2)_{11}COOH$
Polymer: poly(ω-aminolauric acid), nylon-12, $\left[HN(CH_2)_{11}-CO \right]_n$

(b) Monomer: 
Polymer: poly(lauryl lactam), nylon-12, $\left[HN(CH_2)_{11}-CO \right]_n$

(c) Monomer: 
Polymer: poly(ethylene oxide), $\left[CH_2-CH_2-O \right]_n$
or poly(ethylene glycol), $HO\left[CH_2-CH_2-O \right]_n H$

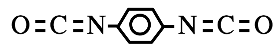
(d) Monomer: 
Polymer: poly(oxacyclobutane), $\left[CH_2-CH_2-CH_2-O \right]_n$

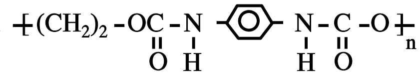
(e) Monomer: $HOCH_2CH_2OH$ and 

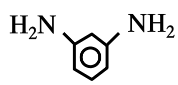
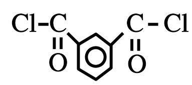
Polymer: poly(ethylene terephthalate), 

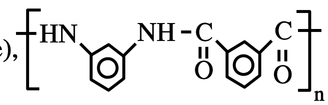
(f) Monomer: $H_2N(CH_2)_6NH_2$ and $HO-\underset{\substack{\| \\ O}}{C}-(CH_2)_8-\underset{\substack{\| \\ O}}{C}-OH$

Polymer: poly(hexamethylene sebacamide), nylon6,10, $\left[HN-(CH_2)_6-NH-\underset{\substack{\| \\ O}}{C}-(CH_2)_8-\underset{\substack{\| \\ O}}{C} \right]_n$

(g) Monomer: $HOCH_2CH_2OH$ and 

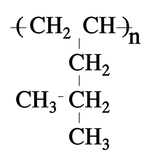
Polymer: poly(ethylene phenylene urethane), 

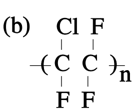
(h) Monomer:  and 

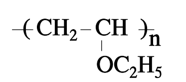
Polymer: poly(m-phenylene isophthalamide), 

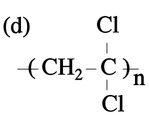
E1.2 Draw the structural formula (one repeating unit) for each of the following polymers : (a) poly(4-methylpent-1-ene); (b) poly(chlorotrifluoroethylene); (c) poly(vinyl ethyl ether); (d) poly(vinylidene chloride); (e) polyethyleneimine; (f) poly(methyl-2-cyano-acrylate); (g) polychloroprene; (h) poly(butylene terephthalate); (i) poly(1,2-propylene oxalate); (j) poly(dihydroxymethylcyclohexyl terephthalate); (k) polycaprolactam (nylon-6); (l) polyformaldehyde; (m) poly-oxymethylene; (n) poly(propylene oxide); (o) poly (propylene glycol); (p) poly(*p*-phenylene sulfone); (q) poly(dimethyl siloxane); (r) poly (vinyl butyral); (s) poly (*p*-phenylene); (t) poly(*p*-xylylene); (u) polycaprolactone

Answer:

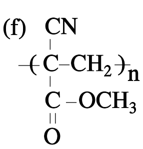
(a) 

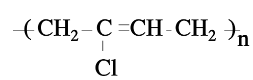
(b) 

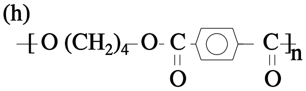
(c) 

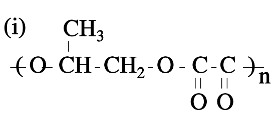
(d) 

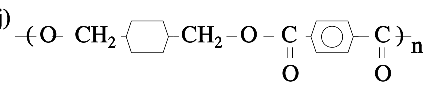
(e) $-(CH_2-CH_2-NH)_n-$

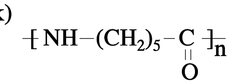
(f) 

(g) 

(h) 

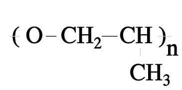
(i) 

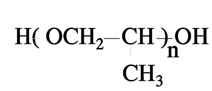
(j) 

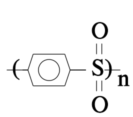
(k) 

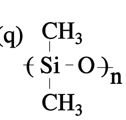
(l) $-(CH_2-O)_n-$

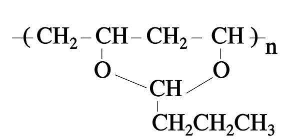
(m) $-(CH_2-O)_n-$

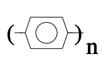
(n) 

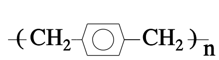
(o) 

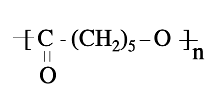
(p) 

(q) 

(r) 

(s) 

(t) 

(u) 

E1.3 What is the degree of polymerization of each of the following polymers with molar mass 100,000 g/mol ?
(a) polyacrylonitrile
(b) polycaprolactam
(c) poly(trimethylene ethylene-urethane)

Answer:

(a) Repeat unit (mer): $–CH_2CH(CN)–$ or C_3H_3N
Mer weight = 3×12 + 3×1 + 1×14 = 53
Degree of polymerization (DP) = 100,000/53 = 1887

(b) Mer: $–NH(CH_2)_5CO–$ or $C_6H_{11}NO$
Mer weight = 113
DP = 100,000/113 = 885

(c) Mer: $-\!\!\left[OCH_2CH_2CH_2OCONHCH_2CH_2NHCO\right]_n\!\!-$ or $C_7H_{12}N_2O_4$
Mer weight = 188
DP = 100,000/188 = 532

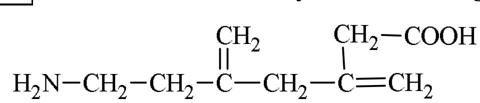
E1.4 What is the functionality of the following monomers in reaction with (a) methyl methacrylate and (b) ethylene glycol ?
(i) Divinyl benzene
(ii) Maleic anhydride
(iii) Phthalic anhydride
(iv) Acrylic acid

Answer:

(a) In reaction with methyl methacrylate, the functionalities of the monomers are:
(i) 4 (two reactive, carbon-carbon double bonds)
(ii) 2 (one reactive, carbon-carbon double bond)
(iii) 0 (anhydride group nonreactive)
(iv) 2 (one reactive carbon-carbon double bond)

(b) In reaction with ethylene glycol, the reactivities of the monomers are:
(i) 0 (carbon-carbon double bonds nonreactive)
(ii) 2 (one reactive anhydride group, which is equivalent to 2 carboxylic acid groups, each of functionality 1; carbon-carbon double bond nonreactive)
(iii) 2 (one reactive anhydride group of functionality 2)
(iv) 1 (one reactive carboxylic acid group; carbon-carbon double bond nonreactive)

E1.5 What is the functionality of the following monomer



(a) in a free radical or ionic addition reaction through C = C double bonds,
(b) in a reaction that produces amide linkages,

(c) in a reaction that produces ester linkages ?

Answer:

(a) The functionality of the monomer is 4 due to the two C=C bonds.
(b) Since both –NH_2 and –COOH groups take part in amide forming reactions, the functionality of the monomer is 2.
(c) The functionality of the monomer is 1 due to one –COOH group.

E1.6 What is the acid value of polycaprolactam (nylon-6) with average *DP* 500 ? [*Note*: Acid value or acid number is defined as the number of milligrams of KOH required to neutralize 1 g of polymer.]

Answer:

Polycaprolactam: H$\text{–}\!\!\!\left[\text{NH–}(CH_2)_5\text{CO}\right]\!\!\!\text{–}_{500}$OH
Formula weight of repeating unit ($C_6H_{11}NO$) = 113 g mol^{-1}
Average molar mass of polymer containing one acid equivalent = 500×113 + 18 or 56,518 g mol^{-1}
Molar mass of KOH = 56 g mol^{-1}

$$\begin{aligned}\text{Acid number} &= \frac{(56 \text{ g mol}^{-1})(1000 \text{ mg/g})}{(56{,}518 \text{ g mol}^{-1})} \\ &\simeq 1\end{aligned}$$

E1.7 How would you determine experimentally whether the polymerization of an unknown monomer was proceeding by a step or a chain mechanism ?

Answer:

Experimentally, the nature of polymerization can be determined by measuring the average molecular weight of the polymer formed as a function of monomer conversion (Fig. E1.7). The average molecular weight builds up slowly in the step polymerization process, and a high-molecular-weight product is formed only after a sufficiently long reaction time when the conversion is more than 98% [see Fig. E1.7(a)]. In contrast, polymerization by chain mechanism proceeds very fast, a full-sized polymer molecule being formed almost instantaneously after a chain is initiated; the polymer size is

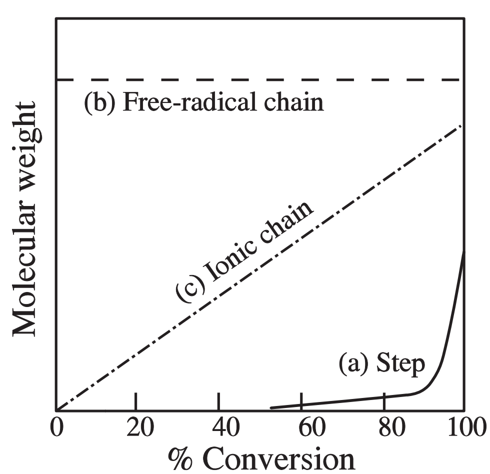
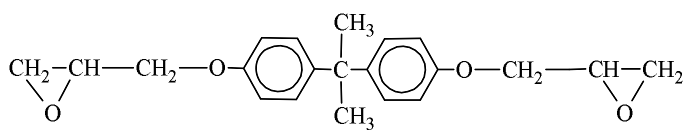


Figure E1.7 Variation of molecular weight with conversion in (a) step polymerization, (b) free-radical chain polymerization, and (c) ionic chain polymerization.

thus independent of reaction time [see Fig. E1.7(b)]. In certain ionic chain polymerizations, which feature a fast initiation process coupled with the absence of reactions that terminate the propagating reactive centers, molecular weight increases linearly with conversion [see Fig. E1.7(c)]. Other differences between step-growth and chain polymerizations are evident from a comparison presented in Table 2.1 (polymer text).

It should be mentioned that the chain plymerizations in the above discussion refer only to conventional free-radical and ionic chain polymerizations. More recently, polymer chemistry has seen the advent of living/controlled free-radical polymerizations involving reversible chain termination or transfer, in which, under suitable conditions, the molecular weight increases linearly with monomer conversion. Four principal mechanisms of living/controlled free-radical polymerization have been discovered. These are alkoxyamine-initiated or nitroxide-mediated polymerization, polymerization with reversible termination by ligand transfer to a metal complex (usually abbreviated as ATRP), polymerization with reversible chain transfer (also termed *degenerative chain transfer*), and polymerization with reversible additio/fragmentation chain transfer (RAFT). These methods have been described in Chapter 11 of polymer text.

E1.8 (a) Referring to the epoxy-amine reaction shown in Fig. 1.7 (polymer text), determine the functionality of the diglycidyl ether of bisphenol A **(I)** in a hardening reaction with diethylene triamine **(II)**.



(I)

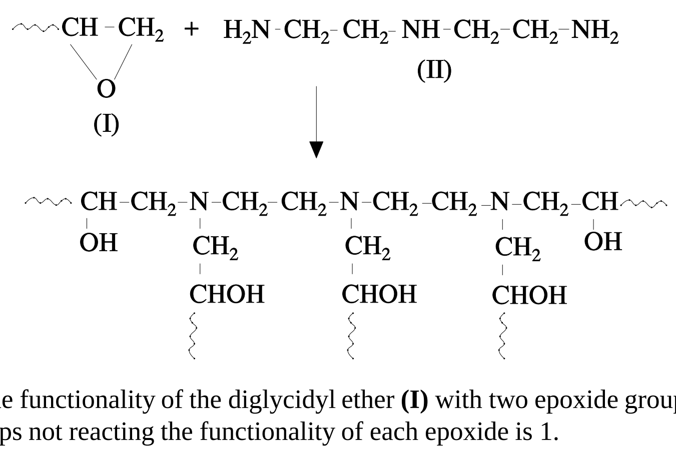
$$H_2N-CH_2-CH_2-NH-CH_2-CH_2-NH_2$$

(II)

(b) What is the functionality of **(II)** in this reaction?

Answer:

(a) With a primary or secondary amine like **(II)** the main reaction is



In this reaction, the functionality of the diglycidyl ether **(I)** with two epoxide groups is 2, since with the hydroxyl groups not reacting the functionality of each epoxide is 1.

(b) The functionality of **(II)** is 5 since there are 5 active hydrogens on the nitrogens.

E1.9 Each of the following polymers can be synthesized from different monomers

(a) $-\!\!\left[O(CH_2)_5CO \right]_n\!\!-$

(b) $-\!\!\left(OCH_2CH_2CH_2 \right)_n\!\!-$

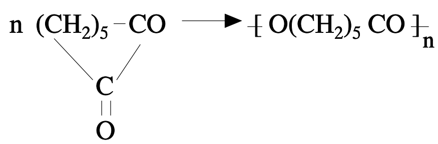
(c) $-\!\!\left[NH{-}(CH_2)_7{-}CO \right]_n\!\!-$

Show by equations the overall chemical reactions involved in the synthesis of these polymers from different monomers.

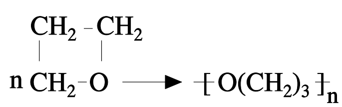
Answer:

(a)

(i) $n\ HO(CH_2)_5CO_2H \longrightarrow \left[O(CH_2)_5CO \right]_n + (n-1)H_2O$

(ii) 

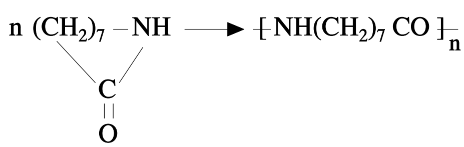
(b)

(i) 

(ii) $n\ Br(CH_2)_3ONa \longrightarrow \left[O(CH_2)_3 \right]_n + (n-1)NaBr$

(c)

(i) $n\ H_2N(CH_2)_7COOH \longrightarrow \left[NH(CH_2)_7CO \right]_n + (n-1)H_2O$

(ii) 

E1.10 Classify the polymers in Exercise E1.1 as to whether they are condensation or addition polymers. Classify the polymerizations as to whether they are step, chain, or ring opening polymerizations.

Answer:

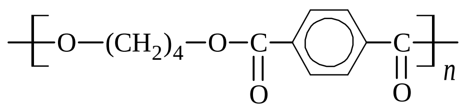
(a) Condensation; step.
(b) Condensation; ring opening.
(c) Condensation; ring opening.
(d) Condensation; ring opening.
(e) Condensation; step.
(f) Condensation; step.
(g) Condensation; step.
(h) Condensation; step.

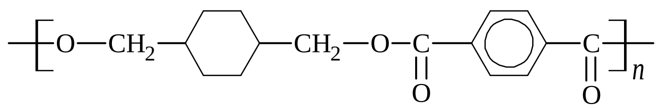
E1.11 Name the polymers obtained in Exercise E1.1 according to their source, i.e., the monomer(s) used in their synthesis.

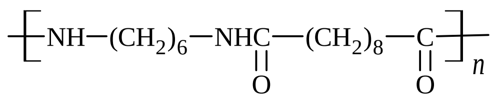
Answer:

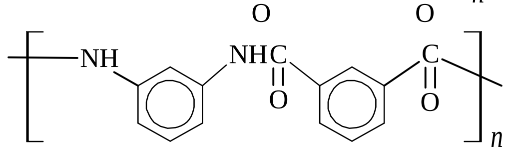
Monomers are mentioned in answers to Exercise E1.1.

E1.12 Name the following condensation polymers according to the common nomenclature

(a) 

(b) 

(c) 

(d) 

Answer:

(a) Poly(tetramethylene terephthalate) or poly(butylene terephthalate); (b) polycyclohexylene terephthalate) or poly(dihydroxymethylcyclohexyl terephthalate); (c) poly(hexamethylene sebacamide); (d) poly(*m*-phenylene isophthalamide).

E1.13 Write repeating formulas and names based on common nomenclature (non-IUPAC) for (a) Nylon-6; (b) Nylon-6,6; (c) Nylon-11; (d) Nylon-6,10; (e) Nylon-5,7.

Answer:

(a) $-[NH-(CH_2)_5-CO]_n-$ poly(6-aminocaproic acid) or poly(ϵ-caprolactam)
(b) $-[NH-(CH_2)_6-NH-CO-(CH_2)_4-CO]_n-$, poly(hexamethylene adipamide)
(c) $-[NH-(CH_2)_{10}-CO]_n-$, poly(ω-aminoundecanoic acid)
(d) $-[NH-(CH_2)_6-NH-CO-(CH_2)_8-CO]_n-$, poly(hexamethylenesebacamide)
(e) $-[NH-(CH_2)_5-NH-CO-(CH_2)_5-CO]_n-$, poly(pentamethylene pimelamide)

Chapter 2

Chain Dimensions, Structures, and Transitional Phenomena

Exercises

E2.1 (a) Calculate the root mean square end-to-end distance and the radius of gyration for a molecule in molten polypropylene of molecular weight 10^5. [Data: carbon-carbon bond length = 1.54×10^{-8} cm; tetrahedral bond angle = 109.5°; steric parameter, σ = 1.6 at 140°C.] (b) How extensible is the molecule? (*Hint:* Calculate the ratio of the extended chain length to the average chain end separation.)

Answer:
(a) Molar mass of repeat unit of polypropylene = 42 g mol^{-1}
Degree of polymerization = (10^5 g mol^{-1})/(42 g mol^{-1} = 2381
Number of C–C bonds in the main chain = 2×2381 = 4762

From Eq. 2.8 (polymer text):

$$\begin{aligned}\langle r^2\rangle_0 &= \sigma^2 n l^2\left(\frac{1-\cos\theta}{1+\cos\theta}\right)\\ &= (1.6)^2(4762)(1.54\times10^{-8}\text{ cm})^2\frac{(1+1/3)}{1-1/3)}\\ &= 5.78\times10^{-12}\text{ cm}^2\end{aligned}$$

RMS end-to-end distance, $\langle r^2\rangle_0^{1/2} = 2.4\times10^{-6}\text{ cm} = 240\text{ Å}$
From Eq. 2.4 (polymer text):

$$\begin{aligned}\text{Radius of gyration, }\langle S^2\rangle^{1/2} &= \langle r^2\rangle_0^{1/2}\ \sqrt{6}\\ &= 2.4\times10^{-6}\text{ cm}/\sqrt{6}\\ &= 9.8\times10^{-7}\text{ cm (= 98Å)}\end{aligned}$$

(b) The most highly extended form involves the all-*trans* conformation of the polymer backbone: