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# Thermoplastic Elastomers



3rd Edition

HANSER

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## Dedication

The original organizer of this work was Dr. N. R. Legge. He also served as an editor for the first two editions. Dr. Legge was best known as the leader of the Shell team that discovered and developed the styrenic thermoplastic elastomers. In 1987 the Rubber Division of the American Chemical society award him the Charles Goodyear Medal for this and other achievements. He recently passed away and this new edition is dedicated to his memory.

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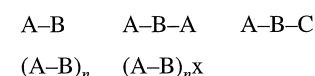
# 1 Introduction

G. Holden, Roderic P. Quirk, Hans R. Kricheldorf

The editors had a number of reasons for bringing forth this Third Edition of Thermoplastic Elastomers. Previous editions were published in 1987 and 1996. Since then there have been many developments. As will be discussed in Chapter 20, growth of the thermoplastic elastomer industry continues. Thermoplastic elastomers have reached a high level of commercial importance, involving many new products and industrial participants. In addition, they have much potential for academic and theoretical research and have attracted a large number of strong academic research groups. From the discovery of the elastomeric character of plasticized PVC in 1926 by Waldo Semon, and the first academic work on block copolymers by Bolland and Melville in 1938, through the discovery of the polyurethanes by Otto Bayer, and all the practical industrial thermoplastic polyamides of the 1930s and 1940s, to the contributions of Flory, Mark, Tobolsky, and many others, there has been an interaction of academic and industrial research enlivened by serendipitous discoveries, which resulted in great advances. Thus we note that since 1967, the date of the first symposium on block copolymers [1]—a symposium largely devoted to the polystyrene/polydiene type—numerous texts [2–21], symposia [22–39], and review articles [40–54] have been devoted either to block copolymers or to the related subject of thermoplastic elastomers.

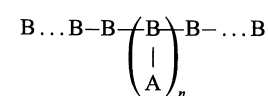
Most thermoplastic elastomers are block or graft copolymers, and here we include a note on their nomenclature. The most commonly applied terminology for block polymers uses A to represent a block of A mer units and, similarly, B, C, etc. to represent blocks of B mer and C mer units and so forth.

The following representations are widely used:



Here, A-B represents a diblock polymer, A-B-C represents a triblock polymer in which all three segments are polymerized from different monomers, and A-B-A represents a block copolymer with two terminal A blocks and a B center block.  $(\text{A-B})_n$  represents an alternating block copolymer, A-B-A-B-A-... etc., whereas  $(\text{A-B})_{n,x}$  represents a branched block copolymer with  $n$  branches ( $n = 2, 3, 4, \dots$ ) and a junction point  $x$ .

Similarly, graft copolymers may be represented as



This represents a polymer in which each B block has (on average)  $n$  random grafts of A blocks.

It is common to use the first letter of the monomer unit to denote the polymer block. For example, a three-block copolymer, poly(styrene-*b*-butadiene-*b*-styrene) is written as S-B-S. If one of the blocks is itself a copolymer (e.g., ethylene-propylene rubber), the block copolymer poly(styrene-*b*-ethylene-*co*-propylene-*b*-styrene) is written as S-EP-S.