

Ethylene-Propylene Copolymers:

Some Aspects of Thermal- and Photo-degradation and Stabilization

R. Mani, R.P. Singh and S. Sivaram

Ethylene-propylene (EP) copolymers exhibit diverse degradation behaviour under the influence of heat and light. This paper briefly reviews some aspects of thermal- and photo-degradation and stabilization of EP copolymers. The chemical and mechanistic aspects of degradation are emphasized. This understanding is especially critical in multiphase polymers such as high-impact heterophasic copolymers, thermoplastic elastomers and blends. Aspects of stabilization relevant to EP copolymers, with special reference to hindered-amine light stabilizers, are discussed.

The diversity of structural variants in polyolefins that one can obtain by the use of two inexpensive monomers, namely, ethylene and propylene, through the use of Ziegler-Natta catalysts and polymerization processes has considerably expanded in recent years. These materials span the full range of polymeric properties, from soft elastomers to hard thermoplastics, depending on the relative composition of ethylene and propylene and the manner of their enchainment¹. The reason for the phenomenal growth of these materials is in large part due to the emergence of new generations of high-efficiency Ziegler-Natta catalysts as well as new process technologies^{2,3}.

In general, olefin copolymers can be broadly discussed in terms of three distinct classes of materials: thermoplastic copolymers; elastomeric copolymers; and thermoplastic elastomers.

Thermoplastic copolymers comprise: statistical copolymers, consisting of propylene, and one or more comonomers such as ethylene and/or but-1-ene at comonomer levels generally lower than 6 mol %; and sequential copolymers, in which propylene is first polymerized and the polypropylene segment subsequently copolymerized with a mixture of ethylene and propylene in a separate reactor, frequently in the gas phase. Polymers produced by this process are heterophasic in nature, in which crystalline polypropylene is the continuous phase and the ethylene-propylene (EP) copolymer is the dispersed elastomeric phase. Since the chain ends of Ziegler-Natta catalysts have only finite life times, true block copolymers cannot be produced by sequential monomer addition. The heterophasic copolymers are mixtures of various fractions of widely differing compositions and crystallinities (X_c) and can be easily fractionated. Table 1 presents data on such systems.

Elastomeric olefin copolymers (ethylene-propylene rubbers, EPR) are amorphous materials that possess rub-

ber-like elasticity and high elongation upon deformation, with an ethylene content typically in the range of 55–65 mol %.

Thermoplastic olefin elastomers (TPO) are a class of polyolefins that possess the processing advantages of thermoplastics combined with the physical properties of chemically vulcanized elastomers. One of the most important commercial TPO is the blend of ethylene-propylene-diene monomer rubber (EPDM) with polypropylene (PP) under conditions where EPDM undergoes crosslinking through the diene moiety⁴. These materials have an interpenetrating network (IPN) morphology (dual phase continuity)⁵.

Typical physical and mechanical properties of different types of olefin copolymers based on ethylene and propylene are given in Table 2. Random EP copolymers containing less than 6 mol % ethylene, are relatively soft materials with low melting points. Copolymers containing 55–65 mol % ethylene are elastomeric in nature with a low glass transition temperature, T_g . Heterophasic copolymers containing <16 mol % ethylene are thermoplastics that show a combination of good impact strength, especially at low temperatures, and excellent rigidity.

By virtue of their very desirable physical, thermal and mechanical properties, EP copolymers are widely used for demanding applications where they are subjected to a variety of forces of degradation. These include outdoor weathering, chemical degradation, environmental stress cracking, mechanochemical degradation and radiation-induced degradation⁶. In broad terms, 'degradation' here implies modification that is often (but not always) detrimental to the performance of the polymeric material.

The mechanisms of thermal- and light-induced degradation and stabilization of olefin homopolymers have been extensively studied⁷. However, corresponding studies of olefin copolymers are of recent origin and have been reviewed recently⁸.

The propensity of polyolefins, especially those containing propylene segments, for thermal and photo-oxidative degradation is well known^{7,9}. The elementary steps in polyolefin degradation are shown in Box 1. As a consequence, inadequately stabilized polyolefins rapidly lose their desirable physical properties. This results in yellowing, loss of impact strength and increased brittleness. The presence of multiple phases of EP copolymers, with different chemical sensitivities to oxidation, introduces an additional degree of complexity in the understanding of the process of degradation. A clearer understanding of the mechanism of degradation in olefin copolymers is also essential for the design of new and more effective

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REVIEWS

Table 1. Fractions from a heterophasic EP copolymer^a

Fraction	Wt%	C ₂ H ₄ ^b (mol %)	Sequence distribution (%) ^c										X _c (%) ^d	T _m (K) ^e	T _g (K) ^e	
			Monads		Dyads			Triads								
			P	E	PP	PE	EE	PPP	PPE	EPE	PEP	EEP				EEE
Whole polymer	–	15.1	84	16	88	2	10	85	2	2	1	3	8	59.8	438.6	–
Xylene insoluble	86	7.7	92	8	93	1	7	93	0	0	0	1	6	63.5	439.7	–
Xylene soluble but acetone insoluble	12	40.9	52	48	30	28	42	24	15	11	8	19	22	<2	–	213

^aEPQ 30R from Himont, Italia, acetone-soluble fraction ~2 wt %.

^bBy FTIR.

^cBy ¹³C-NMR in 1,2-dichlorobenzene at 135°C.

^dBy WAXS.

^eBy DSC.

Table 2. Typical physical and mechanical properties of different types of EP copolymers

Type	C ₂ H ₄ (mol %)	T _g or T _m (°C) (see text)	Crystallinity (%)	Tensile strength (kg cm ⁻²)	Izod impact strength at 25°C (kg cm cm ⁻¹)	Elongation at yield (%)	Flexural modulus (kg cm ⁻²)	Shore A hardness
Random copolymers (thermoplastic)	<6	136 to 148	<50	200–240	2.5–8.0	12–14	6500–10 000	77–84
Random copolymers (elastomeric)	55–65	–50 to –70	<5	650	nr	600 ^a	nr	65
Heterophasic copolymers (thermoplastic)	<16	165 to 170	55–60	200–230	8–12	11–15	13 000–14 000	77–90
Thermoplastic olefinic elastomer	50	na	na	70–140	nb	13–40	<10 000	65–92

^aAt break.

Abbreviations: nr, not relevant; na, not available; nb, no break.

stabilizers, thereby extending the use of EP copolymers to more demanding areas of application.

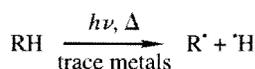
Degradation of EP copolymers

Thermoplastic EP copolymers

A well-characterized heterophasic EP copolymer produced directly in the reactor using the new generation of Ziegler–Natta catalyst has recently been subjected to thermal and photo-oxidative degradation studies^{10–12}. These samples contain 12–15 mol % ethylene and can be easily separated into two fractions, one, highly crystalline, containing 6–7 mol % ethylene and the other pre-

dominantly amorphous, containing 40–55 mol % ethylene (Table 1). The whole and fractionated samples were subjected to thermal (80°C) and photo-oxidation ($\lambda > 295$ nm, 60°C) for varying lengths of time. The progress of degradation was followed by quantitative monitoring of the development of carbonyl and hydroxyl groups using FTIR spectroscopy. To resolve the overlapping bands in the carbonyl and hydroxyl regions more clearly, a technique of derivatization of the photo-oxidized products was employed¹³.

The technique of derivatization involves reaction of carboxylic acid groups with SF₄ to form the corresponding

Box 1. Degradation mechanism in EP copolymers
• Initiation


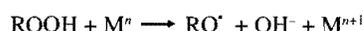
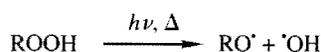
where RH = EP copolymers

• Propagation

Formation of polymer hydroperoxide:



Decomposition of polymer hydroperoxide:

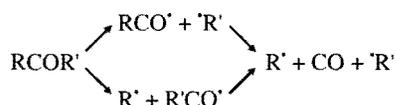


Formation of hydroxyl group:

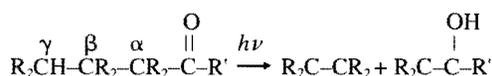
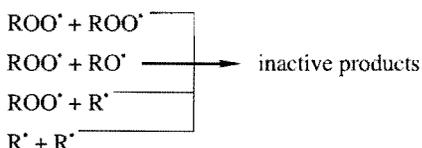


Formation of carbonyl group:

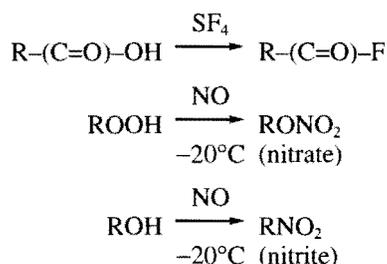
Norrish type I



Norrish type II


• Termination


acid fluoride, and of the hydroperoxides and alcohols with NO to give nitrates and nitrites.



The characteristic IR absorption frequencies of the acid fluorides (1840–1848 cm^{-1}), nitrates (1302 cm^{-1} and 1290 cm^{-1}) and nitrites (778 cm^{-1}) are used to quantify the extent of photo-oxidation. The various bond-break-

ing processes occurring in heterophasic EP copolymers, based on the observed photoproducts, are delineated in Fig. 1.

Micro FTIR spectroscopy has emerged as a powerful analytical tool for the depth profiling of organic functional groups in solid polymers. The combination of imaging, FTIR spectroscopy and quantitative photometry available with micro FTIR spectroscopy allows clear correlation of a polymer's molecular structure with its morphology. The application of this technique to the study of the oxidation process has been described^{14,15}. We have subjected the thermal and photo-oxidized heterophasic EP copolymers to micro FTIR spectroscopy (in a plane perpendicular to the axis of exposure). The film was microtomed in preparation for FTIR investigation and measurements were done for every 45 μm of thickness. The observed profile is a result of the combined effect of diffusion-controlled oxygen permeation and surface crosslinking. This study reveals that whereas photo-oxidation was localized within the first 60 μm , thermal oxidation occurred to a depth of 125 μm (Fig. 2). The elastomeric fraction of the heterophasic EP copolymer did not show any distinctive features in micro FTIR spectroscopy, presumably due to its high oxygen permeability. These results indicate the varying ability of oxygen to diffuse from the surface of the polymer to the bulk depending on the crystalline or amorphous nature of the matrix and the nature of the oxidative process.

From these results it is concluded that, in heterophasic EP copolymers, chain scission by oxidation occurs mainly in the amorphous regions of the polypropylene phase. The amorphous ethylene-propylene rubbery phase remains largely unaffected by oxidation.

EPR copolymers

The degradation of elastomeric EP copolymers has been widely studied in the literature⁸. It has been established that a Norrish type II reaction is mainly responsible for photo-oxidation by chain scission. In these elastomers, the isolated hydroperoxides appeared on the PP unit surrounded by PE sequences and the associated hydroperoxides are formed on the PE segments. The rate of hydroperoxidation increases with increasing propylene content in the copolymer.

A recent paper reports the study of the dependence of elongation at break of an EP elastomer on temperature and oxygen pressure¹⁶. The importance of oxygen pressure as an accelerator in thermal oxidative degradation is revealed. Oxygen diffusion into the EP elastomer determines the activation energy of the degradation process. Maximum absorption of oxygen was observed at 363 K and an oxygen pressure of 2 bar, beyond which the uptake of oxygen ceased. The photo-oxidation of both EP and EPDM copolymers was studied by Maecker and Priddy¹⁷, in both the presence and absence of a hindered-amine-type light stabilizer (HALS-1) (Fig. 3a). Whereas the light stabilizer greatly retarded the rate of photo-oxidation in the case of EP rubber, the effect was less dramatic in the case of EPDM (containing 9% ethylidene norbornene as the diene monomer), which became insoluble after a short exposure time due to crosslinking. Based on an analysis of the evolved volatile component (predominantly acetone), it was proposed that chain scission was the predominant degradative pathway (β -scission of a

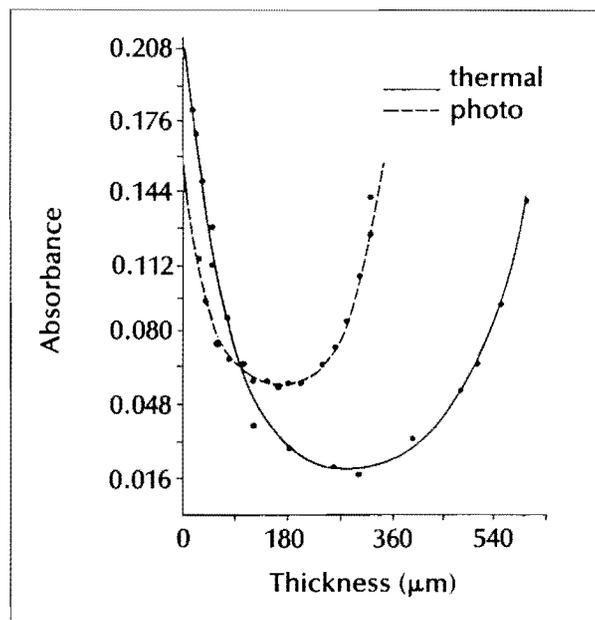


Fig. 2 The distribution of carbonyl groups as a function of thickness for a heterophasic EP copolymer after 50 h of thermal and photo-oxidation.

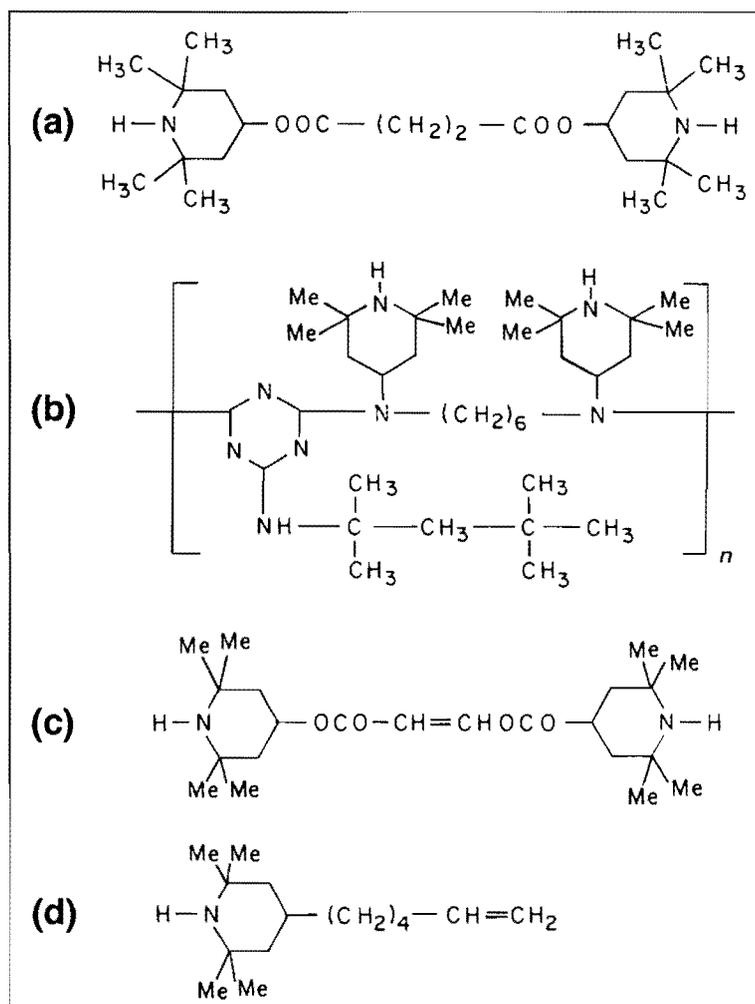


Fig. 3 The structures of hindered-amine light stabilizers (HALS): (a) bis(2,2,6,6-tetramethyl-4-piperidinyl)sebacate (Tinuvin 770); (b) polymeric HALS with $M_n > 2500$ (Chimassorb 944); (c) bis(2,2,6,6-tetramethylpiperidin-4-yl)maleate; and (d) 4-(hex-5-enyl)-2,2,6,6-tetramethylpiperidine.

t-alkoxy radical or Norrish II reaction of a polymeric ketone). In the case of EPDM, it was concluded that the ethylidene group is the precursor to the major volatile products, namely, acetic acid and acetaldehyde.

Stabilization of EP copolymers

Protection of a polymer against thermal and photo-oxidative degradation is achieved by blending the polymer with appropriate stabilizers, which ensure that the desirable polymer properties are maintained throughout its entire service life. During the past decade, the chemistry of synthesis of stabilizers and their mechanism of action have been extensively studied. The interaction between the polymer and stabilizer at a molecular level has been elucidated⁸.

Hindered phenols and secondary aromatic amines belong to the family of antioxidants that inhibit oxidation by a chain-breaking antioxidant mechanism. Chain-breaking antioxidants are those that retard the oxidation by intercepting either R^{\bullet} or ROO^{\bullet} free radicals that propagate the kinetic chain. Trivalent phosphorus compounds and organic compounds of sulfur belong to the family of antioxidants that act by decomposing hydroperoxides. Frequently used light stabilizers belong to the hydroxy-benzophenone, benzotriazole or hindered-piperidine class. The mechanisms of action of various families of stabilizers have been reviewed recently¹⁸ and are given in Box 2.

Under a number of environmental conditions, stabilizers, which are generally low molecular weight organic compounds, are lost by evaporation and leaching, thus rendering the polymer vulnerable to thermal and photo-oxidation. Leaching is of serious concern with respect to both the environment and human health. Thus, apart from its effectiveness, aspects such as solubility and compatibility, as well as diffusion rates from the bulk to surface, need to be assessed when choosing a stabilizer. These aspects become particularly relevant for a multiphase polymer, like a heterophasic EP copolymer, where the stabilizer can partition between different phases in the system. The actual stabilizer concentration in either the elastomeric or thermoplastic phase may differ very significantly from the average total stabilizer concentration in the polymer. In such systems, knowledge of the phase that is more prone to degradation is essential for efficient stabilization to be assured.

Hindered-amine light stabilizers (HALS) have gained prominence in recent years as very effective light stabilizers for a variety of polymers, including polyolefins. The photostabilizing mechanisms of HALS have been reviewed¹⁹⁻²¹. Apart from light stabilization, they exhibit useful functions as retarders of oxidative chain reactions and radical scavengers (Box 2). HALS with molecular weights up to 3500 are commercially available which increases the persistence of stabilizer in the polymer.

To further improve the permanence of the stabilizer in the polymer, a wide range of oligomeric and polymeric stabilizers have been synthesized and evaluated²². For a blend of isotactic-PP and EPR, a mixture of low and high molecular weight HALS (HALS-1 and HALS-2, Fig. 3a and 3b) was found to be superior, doubling the service life under accelerated aging when compared to low molecular weight HALS-1 alone²³.

Surface grafting offers another attractive technique for attaching a stabilizer to the polymer in a permanent manner^{24,25}. Recently, Al-Malaika *et al.* have achieved a high level of grafting of a HALS-type stabilizer (Fig. 3c) onto polyolefins using reactive processing techniques²⁶⁻²⁸.

Synthesis of a stabilizer with a polymerizable group, and its copolymerization with suitable monomers, enables chemical attachment of the stabilizer to the polymer. For example, 4-(hex-5-enyl)-2,2,6,6-tetramethylpiperidine (Fig. 3d) was prepared and copolymerized with propylene using a $\text{TiCl}_4\text{-MgCl}_2\text{-Et}_3\text{Al}$ Ziegler-Natta catalyst system. The copolymer exhibited superior thermal oxidative stability even after exhaustive extraction with boiling heptane²⁹.

Conclusions

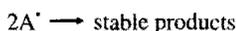
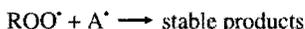
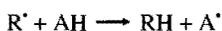
The increasing use of polymers and copolymers in more demanding applications has stimulated research towards a better understanding of their thermal and photo-oxidative degradation behaviour, and a search for effective stabilizers for them. Using a wide variety of analytical tools, it is now possible to probe the fundamental bond-breaking processes that occur upon exposure to heat and/or light, and thereby establish the detailed mechanism of degradation. It is also possible to establish the dependence of critical physical properties of the material on the nature of the chemical changes occurring in the polymer. This has enabled a more rational correlation of laboratory aging data under accelerated conditions with actual weathering in the environment. Nevertheless, the complexity of the degradation process is such that we are still far away from a *de novo* design of stabilizers based on the mechanism of degradation alone. Empirical concepts will continue to play a dominant role in achieving practical stabilization of polymeric materials for diverse end applications.

EP copolymers undergo facile thermal and photo-degradation resulting in rapid loss of useful properties. Such degradation is a function of the polymer composition, structure and morphology. Heterophasic EP copolymers degrade by oxidative chain scission occurring mainly in the amorphous region of the polypropylene phase. Elastomeric EP copolymers also degrade by chain scission whereas EPDM degrades by crosslinking. Depth profiling of oxidative products using micro FTIR spectroscopy shows that, in crystalline fractions of the heterophasic EP copolymers, photo-oxidation occurs up to a depth of 60 μm whereas thermal oxidation occurs up to 120 μm . Although recent research has outlined the myriad bond-breaking reactions in EP copolymers and has identified the phase that is predominantly responsible for degradation, much still remains to be understood. For example, we still do not have any clue regarding the morphological changes occurring in the dispersed and continuous phases of heterophasic EP copolymers. We appear to have no analytical methods that can quantify the concentration of additives dispersed in the two phases.

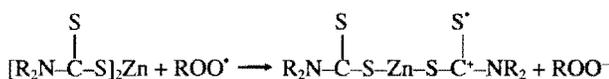
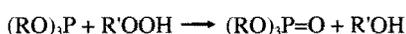
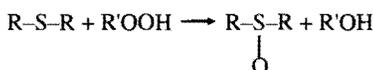
Greater use of multiphase copolymers, including blends and alloys, in demanding engineering applications has stimulated studies aimed towards understanding their degradation and stabilization³⁰. However, there is still a lack of general understanding of the relationship between polymer morphology and the aging process as well as the distribution of additives between multiple phases.

Box 2. Stabilization mechanisms in polyolefins

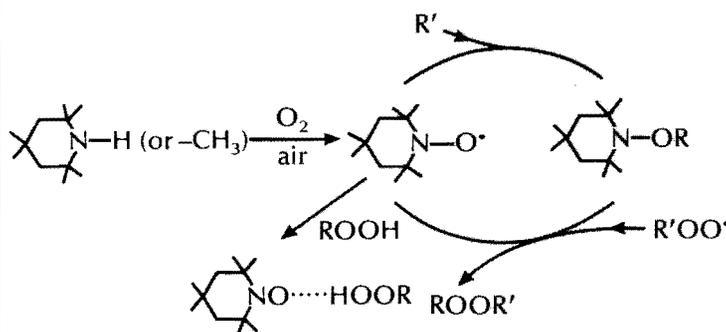
(a) Antioxidants (phenols/amines)



(b) Peroxide decomposers (S/P compounds)



(c) HALS



The ability to target stabilizers to the polymer phase that needs them most, with subsequent control of migration and volatilization, will require new approaches to both the synthesis of stabilizers and the manner of their incorporation into polymers. Synthesis of polymeric or oligomeric stabilizers, where the polymer/oligomer has specific compatibility with a given phase, is an area that merits study. Similarly, surface grafting and reactive processing in an extruder as a means to chemically anchor the stabilizer to the polymer is of considerable interest. This latter technique is especially suitable for incorporating reactive stabilizers in blends and/or alloys. New analytical techniques will be required for estimating stabilizer concentration in multiphase systems and to study stabilizer diffusion/concentration profiles as well as to investigate additive-polymer and polymer-polymer interactions³¹.

Acknowledgements

We thank the Indo-French Centre for the Promotion of Advanced Research (Centre Franco-Indien pour la Promotion de la Recherche Avancée) for financial support of this work through grant No. 308-6. RM thanks the Council of Scientific and Industrial Research, New Delhi, for a research fellowship. We thank Professors J. Lemaire and J. Lacoste of the University of Blaise Pascal, Clermont-Ferrand, France, for generously providing some of the laboratory facilities and stimulating discussions.

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Forthcoming Trends

The topics that will be covered in forthcoming issues of *Trends in Polymer Science* include:

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- Neutron reflectometry and polymer interfaces
- Electropolymerization of olefinic monomers
- Novel polyisobutylene-based biomaterials
 - Light-sensitive polypeptides
 - Polycarbosilanes
- Resists in electron-beam lithography
 - Carbohydrate development
- Molecular modelling of polymers in inclusion compounds
 - The captodative effect in polymer science
- Analysis of high-mass polymers using MALDI mass spectrometry
 - Electric-field induced changes in odd-numbered nylons
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 - Semiconducting polymers
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