

Polyolefin vitrimers and the pseudo-vitrimer concept in semicrystalline polyethylene: A critical review and future perspectives

Farzaneh Rahiminezhad¹, Shervin Ahmadi¹, Hassan Arabi¹, Abbas Tcharkhtchi²

¹Iran Polymer and Petrochemical Institute, 14977-13115 Tehran, Iran

²Emeritus at Arts et Métiers Institute of Technology, CNRS, CNAM, PIMM, HESAM University, 75013 Paris, France

Received: 17 July 2026, Revised: 26 August 2026, Accepted: 17 October 2026

DOI: 10.22063/poj.2026.35899.1397

ABSTRACT

Vitrimer chemistry combines network stability with melt reprocessability through dynamic covalent exchange. Extending this to semicrystalline polyolefins is difficult: their backbones are chemically inert, and their morphology adds structural constraints that most vitrimer systems never have to deal with. Polyolefins are among the most demanding substrates for vitrimer design. Reactive functional groups are scarce along the backbone, and crystallinity complicates both the introduction of dynamic chemistry and the interpretation of the resulting rheology. This review examines recent work on polyethylene- and polypropylene-based vitrimers, focusing on reactive processing, molecular architecture, and semicrystalline morphology as coupled factors governing stress relaxation. On this basis, we propose the concept of a pseudo-vitrimeric state: a vitrimer-like rheological response that arises in certain advanced polyethylene of raised temperature resistance (PE-RT) materials from molecular architecture and semicrystalline morphology, without dynamic covalent bond exchange. Long-chain branching and tie-molecule connectivity appear to be the main contributors, retarding relaxation through physical and topological constraints rather than chemical ones. We also outline an experimental framework that combines rheological measurements with structural characterization to distinguish topology-controlled relaxation from relaxation associated with genuine vitrimer chemistry.

Keywords: Polyolefin vitrimer; PE-RT; reactive extrusion; long-chain branching; polymer topology; semicrystalline morphology.

INTRODUCTION

Dynamic covalent exchange provides an established route to combining the dimensional stability of a thermoset with the reprocessability of a thermoplastic. In associative systems, exchange occurs under a defined stimulus, such as heat, while the network remains connected throughout [1,2]. This mechanism underlies vitrimer chemistry and has since been applied to epoxies, polyesters, polyurethanes, and other polymer families [3,4]. The shift toward a circular plastics economy has raised the practical demands placed on these materials. A polymer is now expected to retain its performance in service while remaining repairable, recyclable, and suitable for repeated processing. Covalent adaptable networks, including vitrimers, meet part of this demand: network topology reorganizes under a defined stimulus without a complete loss of structural integrity [3,4].

Polyethylene and polypropylene present an additional problem. Their backbones contain almost no reactive sites suitable for covalent exchange [5,6], and both are semicrystalline, while most of the early vitrimer literature dealt with amorphous systems [7,8]. The rheological response of a polyolefin vitrimer, as a result, cannot be interpreted from exchange chemistry alone. The experimental literature bears this out. In advanced polyolefins, stress relaxation depends on molecular architecture, processing history, crystallization, entanglement density, and tie-molecule connectivity, not only on dynamic-bond content [7,8,9]. Whether these structural factors can produce a vitrimer-like response on their own, without dynamic covalent exchange, is still unresolved, and it is the question this review is organized around.

We do not propose a new definition of vitrimer chemistry. Instead, we examine the polyolefin literature from a topology-based perspective and ask whether a heat-resistant polyethylene such as PE-RT can, under specific structural conditions, exhibit a rheological response resembling that of a vitrimer while relying on a different molecular mechanism. We refer to this proposed state as pseudo-vitrimeric and treat it as a testable hypothesis rather than as a new material class.

DYNAMIC POLYMERIC NETWORKS: FROM PERMANENT CROSSLINKS TO ADAPTIVE TOPOLOGIES

The evolution of polymer network design

Thermoplastics can be reshaped repeatedly, but they creep, relax stress, and lose dimensional stability under sustained load. Thermosets provide greater structural stability through permanent covalent crosslinking, at the cost of any subsequent melt processing or repair once curing is complete. Polymer network design has long meant choosing between these two limitations. Resource efficiency and circular material use have raised the stakes on both sides of that trade-off. Network design has shifted, in response, from a permanently fixed structure toward architectures where connectivity changes in a controlled way while useful mechanical properties are retained [4,10]. For this reason, the distinction between networks with permanent crosslinks and those without them is no longer sufficient to describe their processing and long-term behavior. The kinetics and mechanisms by which molecular connectivity changes under thermal or mechanical stimulation provide a more useful basis for comparison, as summarized in Figure 1.

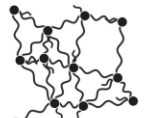
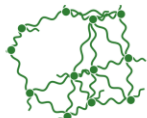
Thermoplastic	Thermoset	CAN	Vitrimer	
No crosslink	Permanent covalent network	Dynamic covalent network	Associative exchange	
				
				
Crosslink type	–	Permanent	Dynamic	Dynamic (associative)
Topology change	No	No	Yes (slow)	Yes (fast above T_v)
Reprocessability	High	None	Limited	High
Creep resistance	Low	High	Medium	High
Self-healing	No	No	Possible	Excellent

Figure 1. Evolution of polymer network design, from permanently crosslinked thermosets through covalent adaptable networks to topology-stabilized semicrystalline systems.

Covalent adaptable networks: A new design philosophy

Covalent adaptable networks (CANs) took a different approach to the conventional split between thermoplastics and thermosets. Their covalent bonds rearrange under an appropriate stimulus while the network as a whole stays connected [1,2], which permits deformation, local repair, and reprocessing without giving up the mechanical benefits of a crosslinked structure. CANs therefore make network architecture an adjustable design variable rather than a fixed property. Their performance depends not only on the presence of covalent junctions but also on the kinetics of junction rearrangement under the relevant processing or service conditions [4,10].

Dissociative and associative dynamic networks

The term CAN covers two mechanistically distinct routes. In dissociative networks, an existing bond breaks before a new one forms, so effective crosslink density drops temporarily during exchange [2]. Associative networks follow a different mechanism: bond formation and exchange occur in a coupled manner as illustrated in Figure 2, so the number of network junctions remains approximately constant while the connectivity changes [3,11]. This distinction is important when interpreting rheological behavior because the transient loss of connectivity characteristic of dissociative exchange is avoided in associative systems. The associative mechanism is central to vitrimer behavior because it allows network rearrangement without requiring complete network disassembly. The resulting combination of dimensional stability and reprocessability distinguishes vitrimers from conventional permanently crosslinked thermosets.

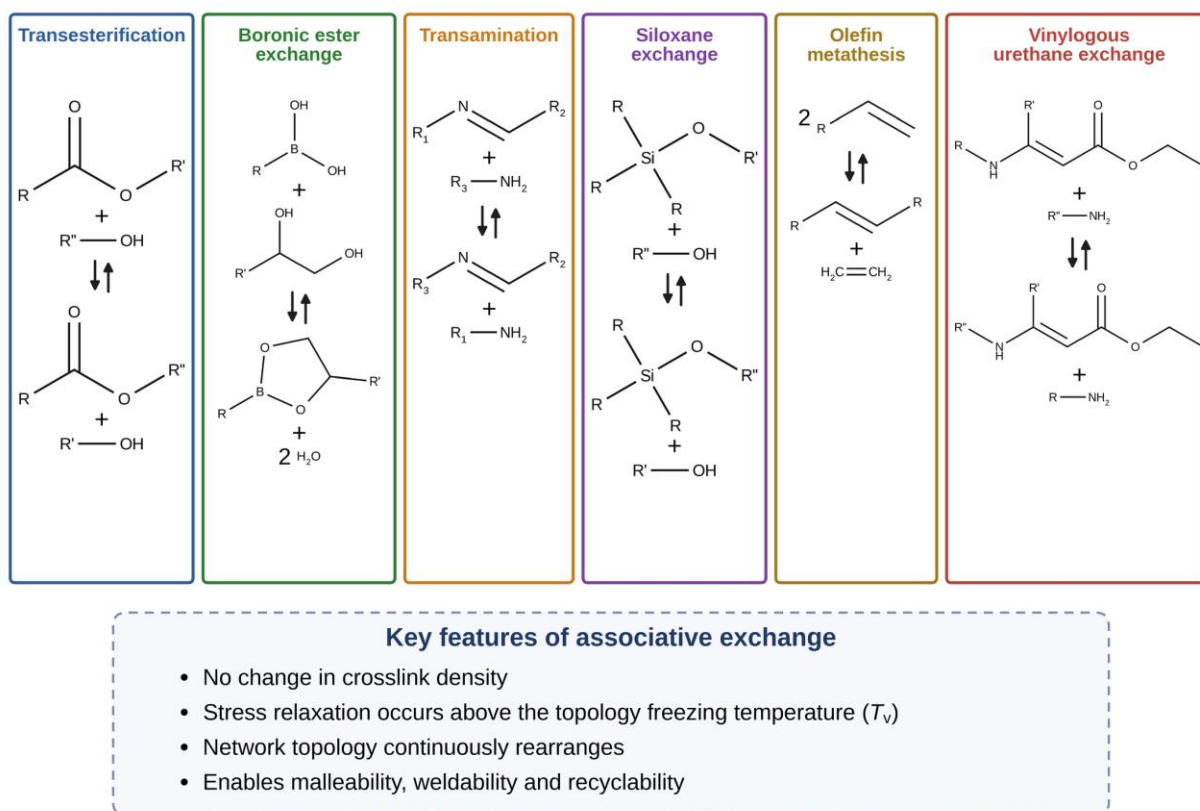


Figure 2. Principal associative dynamic covalent exchange mechanisms used in polyolefin vitrimer systems, including dioxaborolane metathesis, transesterification, disulfide exchange, and silyl ether exchange.

Why vitrimers changed polymer science

Leibler and co-workers introduced the vitrimer concept in 2011 [3]. Its significance went beyond the specific dynamic reaction used: the work gave a framework for understanding how a covalently connected network can flow at all, through continuous associative exchange. In a conventional thermoplastic, flow ultimately involves large-scale chain disengagement. Permanent crosslinks suppress this process in thermosets. In a vitrimer, network connectivity is retained while the topology changes through associative exchange, allowing deformation and flow without complete network breakdown [1,3,11]. This mechanism made it possible to combine dimensional stability with active processing, damage repair through network reconstruction rather than patching, and adhesive-free welding [5,12]. The chemistry subsequently moved from epoxies into polyesters, polyurethanes, vinylogous urethanes [13], silicones [14], polyamides, and polyolefins [5,15].

Variability across chemistries

As the field developed, a limitation of a chemistry-centered interpretation became apparent. Materials based on similar exchange chemistries can show substantially different rheological responses [9,16,17], while some systems without dynamic covalent chemistry exhibit comparatively slow stress relaxation and high creep resistance. Molecular architecture, crystallization, chain entanglement, phase morphology, and processing history all appear to contribute to the measured response [8,18,19]. Polyolefins are a particularly useful test case, since dynamic chemistry is hard to introduce and semicrystalline morphology adds its own

physical constraints. This raises the question of whether some vitrimer-like rheological responses originate mainly from topology and morphology rather than bond exchange.

POLYOLEFIN VITRIMERS: CHALLENGES BEYOND DYNAMIC CHEMISTRY

Why polyolefins represent a unique case

Polyolefins became a logical target for vitrimer research after the concept had been demonstrated in epoxies, polyesters, and polyurethanes. Their industrial scale makes even incremental improvements in recyclability potentially significant, but their chemical structure also creates a more difficult starting point for dynamic-network design. The same properties that make polyethylene and polypropylene useful—an inert backbone, low polarity, and high chemical resistance—also limit the number of sites available for introducing dynamic covalent bonds. Condensation polymers come pre-loaded with reactive groups. Polyolefins have essentially none and must be chemically activated before any vitrimer chemistry can start [5,6], usually by peroxide-assisted grafting, reactive extrusion, post-functionalization, or catalytic insertion polymerization designed specifically for the purpose [15,20,21].

The complexity of semicrystalline polyolefins

Polyolefins are semicrystalline materials, so molecular mobility is constrained by a morphology that is not present in the same form in most early amorphous vitrimer systems. During cooling, chains partition into crystalline lamellae, amorphous interlamellar regions, tie molecules, and entangled domains. These structural populations respond differently to deformation and therefore contribute differently to stress relaxation [7,8]. The rheological response of a semicrystalline polyolefin, as a result, cannot be attributed to covalent exchange alone, even where exchange chemistry has been incorporated into the material. Crystallization, molecular architecture, and topology all contribute at the same time. Creep resistance and thermal dimensional stability can arise partly from these physical constraints, so a relaxation curve on its own is not sufficient evidence of dynamic bond exchange.

Polyethylene as a model system

Polyethylene is a useful model system for this literature because its relatively simple chemical structure allows changes in branching, molecular-weight distribution, crystallinity, and topology to be related to rheological behavior more directly than in polymers with more complex chemistry. Its processing characteristics and established applications in pressure pipes, cable insulation, and geomembranes also make the results industrially relevant [22]. Röttger and co-workers demonstrated that polyethylene could be converted into a dynamically crosslinked network through dioxaborolane metathesis, yielding an insoluble and solvent-resistant material that remained melt-reprocessable and weldable [5]. A subsequent single-step reactive-extrusion route using bis(dioxaborolane) crosslinkers further demonstrated the feasibility of processing such systems [21]. These results showed that solvent resistance and melt reprocessability need not be mutually exclusive. The same studies also reported relaxation times that, in several cases, were slower than would be expected from the exchange kinetics alone [7,9]. Thus far, exchange kinetics alone did not fully account for the relaxation observed.

Table 1 compares the principal polyethylene vitrimer chemistries reported in this area, together with their reported advantages and remaining limitations. Across the systems, several limitations concern morphology, processing, and scale-up rather than the dynamic chemistry itself.

Table 1. Comparison of the principal polyethylene vitrimer chemistries discussed in this section, with their reported advantages, remaining limitations, and their relevance to the topology-controlled relaxation picture developed in this review.

Author(s)	Crosslink chemistry	Key advantage	Key limitation	Relevance to topology-controlled relaxation
Röttger et al. [5]	Dioxaborolane (boronic ester) metathesis	Converts commodity PE directly into a solvent-resistant, weldable, reprocessable network	Rheology dominated by phase-separated crosslink aggregates rather than classical vitrimer kinetics	Illustrates that dynamic exchange alone does not guarantee classical vitrimer kinetics once the network phase-separates; morphology, rather than chemistry, sets the rate-limiting step in this system.
Maaz et al. [21]	Bis(dioxaborolane) crosslinking by single-step reactive extrusion	No small-molecule byproducts; directly compatible with continuous melt processing	Network morphology very sensitive to graft structure and choice of processing aids	Shows that even a chemically well-defined system remains sensitive to graft-level topology, consistent with a topology-linked rather than purely chemistry-linked relaxation picture.
Odenwald et al. [15]	Boronic ester via catalytic insertion polymerization	Homogeneous, chain-end-enriched crosslink distribution; minimal leaching	Requires specialized insertion catalysis rather than post-polymerization grafting	Homogeneous crosslink placement narrows topological variability, making this system a useful reference point for isolating chemical from topological contributions.
Valdez & Qiang [23,24]	Epoxy-crosslinked maleated PE (Zn/Mn catalysis)	Catalyst choice enables tunable lamellar thickness and gel fraction	Higher crosslink density suppresses crystallinity and shifts crystallization kinetics	Links crosslink density directly to lamellar thickness, indicating that chemistry and crystalline topology are not independent variables in this system.
Fenimore et al. [25]	Dialkylamino disulfide, catalyst-free	Applicable to virgin and waste PE without metal catalysts	Reactive-processing scale-up beyond laboratory demonstration remains to be established	Decouples the chemistry from processing scale-up, but does not resolve whether relaxation at larger scale is chemistry- or topology-dominated.

Looking beyond bond exchange

Several structural effects recur across polyethylene vitrimer systems. Dynamic crosslinks tend to form nanoscale domains rather than a uniform distribution [8]. Crystalline lamellae restrict chain mobility [7]. Tie molecules maintain mechanical connectivity between neighboring crystals [26]. Long-chain branching modifies reptation [27,28], and entanglements broaden the relaxation spectrum beyond what a simple exchange model predicts [16]. These observations, together, support a multiscale description in which chemical and physical constraints operate at the same time. Relating vitrimer chemistry to macroscopic rheology means accounting for processing, molecular architecture, topology, and morphology as well [18,19]. Figure 3 illustrates this hierarchical morphology.

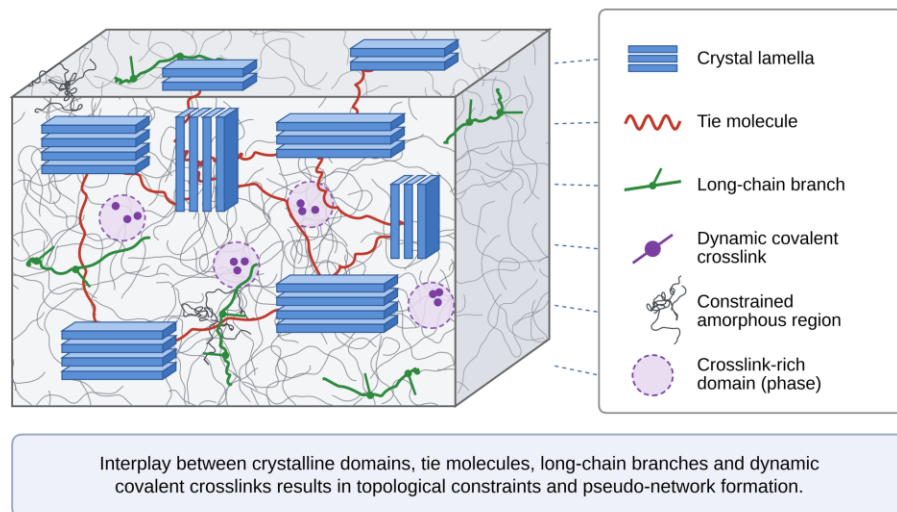


Figure 3. Hierarchical morphology of a semicrystalline polyolefin vitrimer, showing crystalline lamellae, constrained amorphous interphases, tie molecules, and phase-separated dynamic crosslink aggregates coexisting within the same material.

A critical perspective

The central issue is how much of the measured vitrimer-like response originates from dynamic chemistry and how much can be attributed to the physical organization of the polymer. Because semicrystalline morphology and molecular topology already influence stress relaxation, a chemistry-only interpretation is incomplete. Reactive extrusion is particularly relevant because it is one of the stages at which molecular architecture is modified and subsequently carried into the semicrystalline structure.

REACTIVE BLENDING: ENGINEERING POLYMER TOPOLOGY RATHER THAN PROCESSING POLYMERS

Reactive blending reconsidered

Reactive extrusion is commonly defined as melt blending accompanied by chemical reactions. In the context of this review, its importance is broader: the process can modify molecular architecture while the polymer is being shaped, making processing conditions part of the route by which topology is generated [21,29]. In conventional extrusion, molecular architecture is largely fixed before processing starts. Reactive extrusion is different: functionalization, chain recombination, branching, dynamic-junction formation, and chain degradation all occur within the same processing window, so the resulting architecture is tied to the thermal, residence-time, shear, and mixing history the material experienced in the extruder. Under these conditions the extruder functions as a continuous reaction environment, and processing parameters directly set the topology obtained at the die. This matters most for polyolefins, whose backbones need chemical activation before these reactions can occur at all. Figure 4 outlines this reactive-extrusion process schematically.

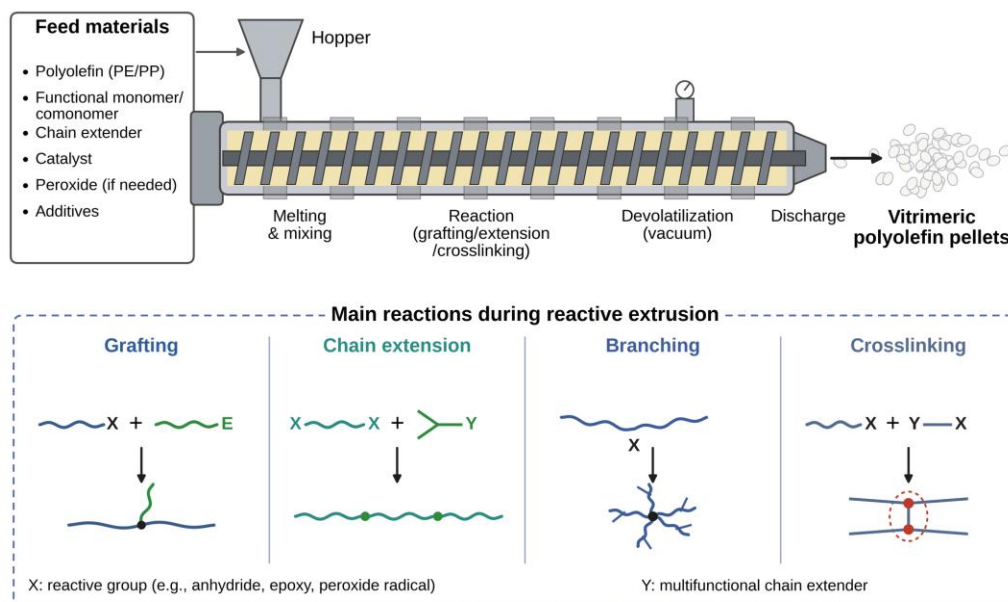


Figure 4. Schematic of reactive extrusion for polyolefin vitrimer synthesis, showing radical generation, grafting, branching and chain extension, and dynamic crosslink formation along the screw.

Competing molecular events during processing

During reactive processing, radical formation, hydrogen abstraction, grafting, chain scission, branching, chain extension, crosslink formation, and oxidation all compete within the same residence-time window [21,25]. Studies of polyolefin elastomers show how real this competition is: functional groups graft efficiently during melt processing [30], and covalently incorporated stabilizers remain compatible with the matrix even after blending [31]. The formulation alone cannot determine the final molecular architecture. Temperature, residence time, shear history, peroxide concentration, catalyst efficiency, and local mixing conditions each pull the reaction balance in a different direction, so identical feedstocks can end up with different rheological properties once processed under different conditions.

Polyethylene and polypropylene respond

Polyethylene and polypropylene are often grouped together as olefinic thermoplastics, but their responses during reactive processing differ. In polyethylene, radical recombination is comparatively favorable, which can promote long-chain branching, chain extension, and limited network formation while keeping degradation manageable under controlled conditions [27,32]. Polypropylene's tertiary carbons make β -scission easy, so degradation competes more aggressively with branching there, and conditions that work well for polyethylene can strip away molecular weight in PP instead [33]. Resonance-stabilized radical intermediates shift that balance by suppressing β -scission and favoring branching [34]. Internally catalyzed transesterification offers another route, one that avoids the need for a separate catalyst altogether [35]. The outcome therefore depends on the interaction between polymer chemistry and processing conditions. Table 2 summarizes the principal polypropylene systems in the same format used for polyethylene; the main limitations differ between the two polymers, with radical control being particularly important for PP and morphology playing a larger role in PE.

Table 2. Comparison of the principal polypropylene vitrimer chemistries, following the same format as Table 1, including their relevance to topology-controlled relaxation.

Author(s)	Crosslink chemistry	Key advantage	Key limitation	Relevance to Topology-Controlled Relaxation
Gao & Niu [35]	Internally catalyzed transesterification (neighboring-group participation)	No external catalyst; simple maleic anhydride + diol chemistry	Crosslink density limited by diol stoichiometry; slower relaxation than catalyzed systems	Relaxation here is limited mainly by network stoichiometry rather than topology, offering a comparatively clean chemical baseline for comparison.
Huang, Torkelson et al. [34]	Resonance-stabilized radical CAN (low-crystallinity propylene–ethylene copolymer)	Suppresses more than 99% of viscous creep at 160 °C; full property recovery after repeated reprocessing	Requires low-crystallinity copolymer feedstock rather than commodity isotactic PP	Strong creep suppression depends on a low-crystallinity feedstock, which limits how directly this result generalizes to semicrystalline commercial PP grades.
Dey et al. [36]	Epoxy-crosslinked maleated PCR-PP	Valorizes post-consumer waste; compatibilizes mixed PE/PP streams	Relies on virgin epoxy crosslinker input; long-term weathering performance not yet reported	Waste-stream heterogeneity introduces topological variability that is difficult to separate from the chemistry, so relaxation likely reflects both factors jointly.

Reactive blending as topology engineering

Reactive extrusion has traditionally been used to introduce chemical functionality into an existing polymer. The same process can also be used to modify molecular topology through chain extension, branching, and controlled network formation. Chain extenders reconnect chains that have degraded, and multifunctional extenders produce branched architectures instead of simple linear reconnections, as demonstrated for poly(ethylene terephthalate) (PET) [37,38]. Local network formation raises molecular connectivity further, and dynamic exchange reactions, where present, keep the topology changing after processing. Subsequent cooling determines how these modified chains crystallize and how tie molecules end up distributed through the semicrystalline structure [32]. Reactive extrusion links chemistry, processing, and molecular architecture in a single step. The reactions set what structural changes are possible; processing conditions determine how far and how evenly they occur; crystallization locks part of the resulting architecture in place. Rheology is simply where all of this becomes visible.

Processing history and long-term behavior

Reactive processing leaves a lasting signature in the semicrystalline architecture of the polymer. Branching architecture, entanglement density, crystalline morphology, and tie-molecule distribution are set during processing and cooling, and once established they constrain how the material subsequently responds to load [22,32]. Long-term creep resistance in advanced PE-RT materials depends, in part, on structural features built in during extrusion, not on chemical composition alone. Processing history is best treated as a material-history variable in its own right when interpreting long-term rheological data.

MOLECULAR ARCHITECTURE AS A DETERMINING FACTOR IN POLYOLEFIN PERFORMANCE

For much of the development of polyolefin technology, molecular weight and molecular-weight distribution were the principal structural variables used to explain performance. Increasing molecular weight generally improves toughness, creep resistance, and melt strength; a broader distribution tends to improve processability. These correlations hold across many commercial grades but do not account for the full range of behavior reported in high-performance polyolefins [39,40]. Materials with similar molecular weight can show substantially different stress relaxation, melt elasticity, strain hardening, and long-term dimensional stability [39,40]. These differences correspond to structural organization not captured by molecular-weight measurements. In commercial resins, where molecular-weight distribution and branching typically vary together, isolating a single cause is difficult.

Attention has shifted, as a result, toward molecular architecture: chain connectivity, branching, entanglement structure, and how these change during processing and crystallization. Long-chain branching and chain extension are relevant rheological variables in their own right, not secondary structural details [27,28]. In amorphous polymers, molecular mobility is governed mainly by chain dynamics. In semicrystalline polyethylene and polypropylene, crystalline lamellae, amorphous regions, tie molecules, and entanglements form a hierarchical structure that governs mechanical response instead. Molecular architecture carries particular weight, for this reason, in interpreting semicrystalline polyolefin behavior. Reconnecting chains that have undergone degradation changes molecular connectivity and the distribution of intermolecular entanglements. Chain extension illustrates this effect: multifunctional extenders can generate branched reconnections rather than simple linear ones. The principle is general across polymer classes: in poly(ethylene terephthalate) (PET), for example, the combination of pyromellitic dianhydride with pentaerythritol produces long-chain-branched structures with increased melt elasticity and strain hardening [40]. This PET example illustrates the chain-extension mechanism only and is not taken as evidence for polyethylene architecture. Among polyolefins, related effects of long-chain branching on rheology and morphology have been reported for polypropylene and its blends [37].

Branch points restrict reptation, raise melt elasticity, and broaden the relaxation spectrum by opening several relaxation pathways at once [27,28]. Short-chain branching mainly affects crystallization; long-chain branching reaches into the dynamics of the whole molecular network, and from there into creep resistance, slow crack growth, and long-term mechanical stability. These effects do not require dynamic covalent exchange. Figure 5 illustrates how branching and chain extension modify the underlying molecular architecture.

Molecular architecture alone can retard relaxation and produce a rheological response substantially different from that of linear polyethylene. This does not make topology equivalent to vitrimer chemistry. It indicates, instead, that comparable macroscopic stabilization can arise through a different molecular mechanism. Chain extension, branching, limited crosslink formation, and crystallization evolve together throughout extrusion [41,42,43], rather than as independent, sequential steps. The architecture produced during processing shapes both subsequent crystallization and how tie molecules end up distributed within the semicrystalline structure [32].

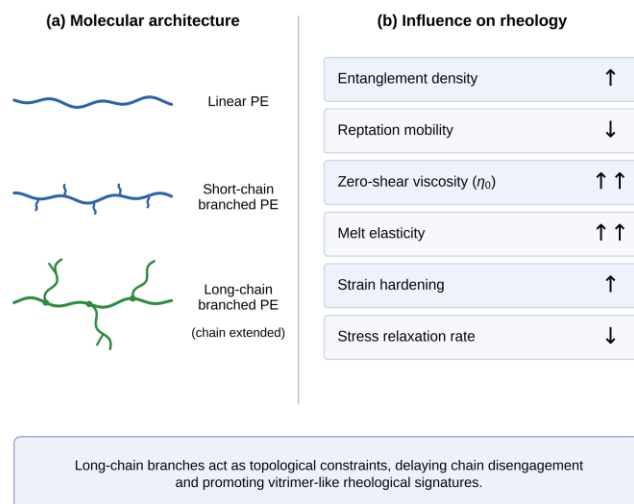


Figure 5. Effect of long-chain branching and chain extension on molecular architecture, showing how branch points and multifunctional reconnection broaden the relaxation spectrum and retard reptation.

SEMICRYSTALLINE MORPHOLOGY AND THE PHYSICAL ORIGIN OF STRUCTURAL STABILITY

The molecular architecture generated during reactive processing survives, in part, through crystallization and gets redistributed across the resulting hierarchical morphology. The final structure reflects both the processing chemistry and the crystallization history the material went through. In a semicrystalline polyolefin, crystallization is not simply a phase transition preceding the final product. It determines how modified chains are partitioned between crystalline and amorphous regions and thereby establishes structural constraints that persist during subsequent deformation.

Crystalline lamellae provide stiffness and dimensional stability, whereas the amorphous phase accommodates deformation and dissipates stress. Between them lies an interphase in which chain mobility changes progressively with distance from the crystalline surface. The resulting heterogeneity contributes to the broad relaxation behavior of semicrystalline polyolefins. Crystallinity has long been recognized as an important determinant of polyethylene stiffness and thermal resistance. It does not explain all of the differences observed between materials with similar overall crystallinity, though, because the distribution and connectivity of the crystalline and amorphous regions affect molecular mobility independently of the crystallinity value itself. How the crystalline and amorphous phases are organized internally is, for this reason, often more informative than the overall crystallinity figure. Table 3 summarizes the main structural populations within semicrystalline polyethylene and their expected roles in the rheological response.

Table 3. Structural populations within semicrystalline polyethylene and the functional role each plays in the rheological response.

Structural population	Functional role
Thick lamellae	Dimensional stability and stiffness under sustained load
Thin lamellae	Flexibility and accommodation of local deformation
Tie molecules	Stress transfer between neighboring crystalline domains
Constrained amorphous phase	Delayed segmental relaxation and broadened relaxation spectrum
Paracrystalline domains	Gradual softening rather than an abrupt mechanical transition

Tie molecules connect neighboring crystalline regions and maintain mechanical continuity across the material, unlike chains confined largely within a single lamella. Their concentration is low, but their contribution to stress transfer is disproportionate, since they couple otherwise separate crystalline domains. Quantifying tie-molecule density directly remains difficult, and most estimates in the literature are inferred indirectly from mechanical or thermal measurements rather than measured structurally. Chain segments close to a crystalline surface have restricted mobility, whereas segments farther from the interface retain greater freedom. The amorphous phase is therefore heterogeneous rather than a uniform reservoir of mobile chains, and this heterogeneity contributes to the breadth of the relaxation spectrum.

Branch points alter crystal growth, lamellar organization, tie-molecule formation, and how entanglements are distributed within the amorphous phase [23, 32]. Long-chain branching, in this way, couples molecular architecture directly to crystallization and makes the resulting morphology more heterogeneous. Crystallization, molecular connectivity, and entanglement restrict chain mobility and delay stress relaxation without any dynamic covalent junction being present. These constraints share no mechanism with bond exchange, yet they produce macroscopic features in rheological measurements that closely resemble it.

RETHINKING VITRIMERS-LIKE BEHAVIOUR IN ADVANCED PE-RT

Evidence for topology-controlled relaxation

Stress relaxation in advanced polyethylene systems does not correlate uniformly with dynamic-bond content. Molecular architecture, semicrystalline morphology, and topological constraint account for a substantial part of the relaxation behavior reported in several systems [7,18]. The established vitrimer mechanism itself is not in question here; associative bond exchange remains the defining feature that separates a vitrimer network from an ordinary thermoset [1,3]. The reported effects of branching, tie molecules, and constrained amorphous regions should not be interpreted independently. Long-chain branching primarily modifies terminal relaxation through its effect on reptation [27,28]. Tie molecules introduce constraints tied specifically to the semicrystalline morphology and sustain stress transfer between crystalline domains [26]. Constrained amorphous regions add a further limitation on segmental motion near crystal-amorphous interfaces [8], and heterogeneous crystalline structures broaden the relaxation spectrum on top of that [44]. In commercial PE-RT materials, where these features change together, separating their individual contributions experimentally is difficult, even though each mechanism is well characterized on its own.

Interplay between molecular architecture and morphology

These mechanisms have largely been studied in isolation: branching in one body of work, tie molecules in another, crystalline heterogeneity in a third. Few studies have examined their combined effect in the same material, and no structural framework in the literature links them jointly to rheological behavior. Without such a framework, assigning a given relaxation feature to a single mechanism is not well justified. Under structural conditions where these constraints act together, a semicrystalline polyolefin may develop rheological stability that resembles several features of a vitrimer network, without reversible covalent bond exchange. The underlying mechanism, in that case, would differ from a conventional vitrimer's. It would depend on the coupled effects of molecular topology and hierarchical morphology rather than on exchange

kinetics. Such a material would not be a vitrimer in the chemical sense, though its macroscopic response could approach that of a dynamically crosslinked network over relevant timescales.

Proposed pseudo-vitrimeric state

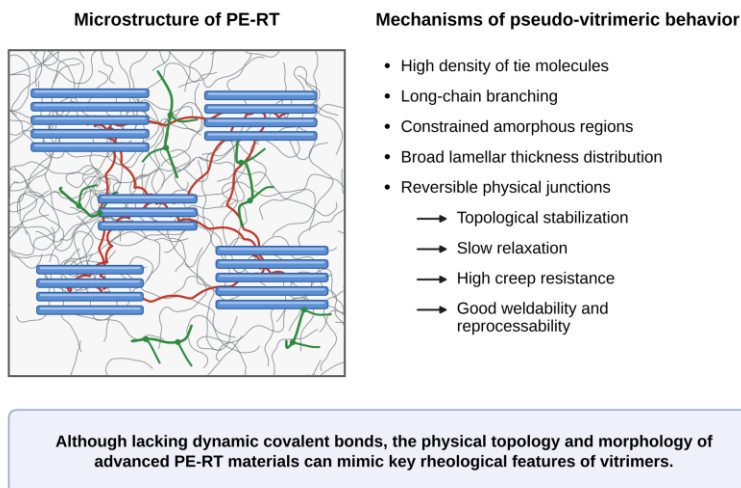
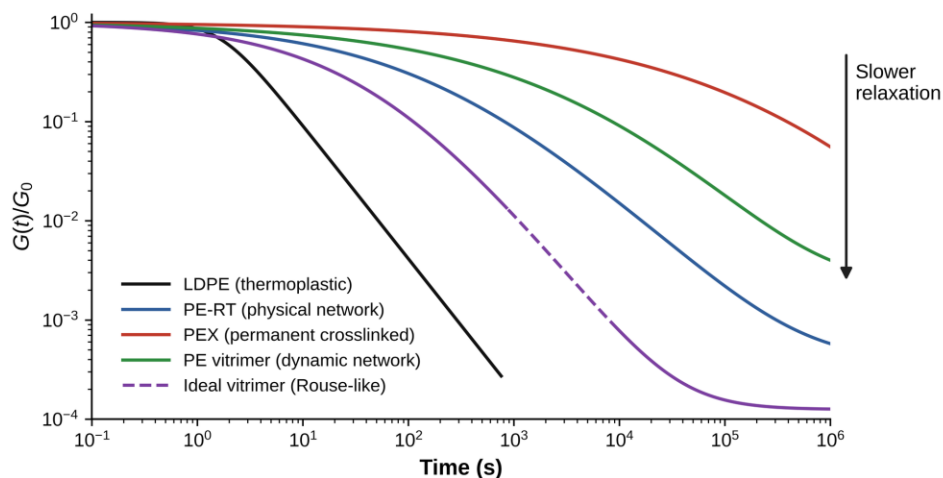


Figure 6. Proposed pseudo-vitrimeric behavior in advanced PE-RT systems, in which long-chain comonomers, tie-chain-rich morphology, and constrained interphases together delay relaxation without any dynamic covalent exchange.

We refer to this proposed structural condition as a pseudo-vitrimeric state, illustrated schematically in Figure 6. The term pseudo-vitrimeric state describes a rheological response rather than a new polymer class, and does not imply that topology can substitute for dynamic covalent chemistry in every aspect of vitrimer behavior. Its scope is limited to a rheological state in which structural organization delays molecular relaxation beyond the range expected for a conventional linear thermoplastic. Table 4 sets out the diagnostic criteria used in this review. This scope is deliberately narrow: the term is not intended to cover any material that happens to relax slowly. Similar macroscopic responses arising from different microscopic mechanisms are documented elsewhere in polymer science, and the same logic applies here.

Pseudo-vitrimeric behavior is accordingly treated as a topology-controlled rheological state rather than a chemical material class, resulting from the combined effects of molecular architecture, entanglement stabilization, tie molecules, constrained amorphous regions, and semicrystalline organization. Figure 7 compares the resulting stress-relaxation behavior across these material classes, and Table 4 sets out diagnostic criteria distinguishing a pseudo-vitrimeric PE-RT from three materials with which it could plausibly be confused: chemically crosslinked polyethylene (PEX), a conventional long-chain-branched polyethylene such as autoclave LDPE, and a genuine dynamic covalent vitrimer. The criteria are strict by design; a material must satisfy all of them to qualify. A resin that relaxes slowly for undetermined structural reasons is more accurately described simply as a creep-resistant thermoplastic.



Vitrimers exhibit a plateau in stress relaxation similar to thermosets at short times, but eventually relax to zero stress above the topology freezing temperature (T_v).

Figure 7. Stress relaxation behavior of different polyolefin materials, contrasting a linear thermoplastic, a long-chain-branched grade, a topology-stabilized PE-RT system, and a true dynamic covalent vitrimer.

Table 4. Proposed diagnostic criteria distinguishing a pseudo-vitrimeric PE-RT from three related but conceptually distinct materials.

Criterion	Physically crosslinked PE (PEX)	Conventional LCB-PE (e.g. LDPE)	Pseudo-vitrimeric PE-RT	True dynamic vitrimer
Covalent network junctions	Yes (permanent)	No	No	Yes (dynamic)
Origin of slow relaxation	Permanent crosslinks	Branch-point drag	Tie-chain and entanglement topology	Bond-exchange kinetics
Melt reprocessability	No	Yes	Yes	Yes (above T_v)
Temperature dependence of relaxation	N/A (does not flow)	WLF	WLF / reptation-controlled	Arrhenius (exchange-controlled)
Solubility in hot xylene	No (insoluble gel)	Yes (fully soluble)	Yes (fully soluble)	No (insoluble, swells)
Dominant creep mechanism	Network elasticity	Chain-retraction resistance	Tie-chain constraint	Exchange-limited flow

Table 5 makes the same comparison from an applications angle, weighing PE-RT against PEX and a polyethylene vitrimer on the properties that actually decide material selection for pressure-pipe and long-life structural work. PE-RT already sits in an odd spot: high reprocessability, although through a different mechanism from a vitrimer, relaxation behavior closer to that of a crosslinked material, without requiring dynamic covalent exchange.

Table 5. Comparison of PE-RT, PEX, and polyethylene vitrimers across the properties most relevant to pressure-pipe and long-life structural applications.

Property	PE-RT	PEX	PE vitrimer
Crosslink type	Semicrystalline / topological constraints	Permanent covalent	Dynamic covalent
Reprocessability	High	None	High
Stress relaxation	Slow	Very slow	Tunable
Melt processability	Excellent	Limited	Moderate
Repairability	Moderate	Poor	Excellent

Structural stabilization in a semicrystalline polyolefin can occur through chemical, physical, and topological routes, summarized in Table 6, and these operate in parallel rather than in competition. Conventional vitrimer research has focused mainly on the chemical route. The argument developed here is that the topological contribution deserves equal attention and, in advanced PE-RT, may make a substantial contribution.

Table 6. A three-dimensional stabilization framework for advanced semicrystalline polyolefins, in which chemical, physical, and topological mechanisms act in parallel.

Stabilization mechanism	Structural origin	Functional consequence
Chemical stabilization	Dynamic covalent exchange chemistry	Reprocessability and self-healing
Physical stabilization	Crystalline lamellae	Dimensional stability and stiffness
Topological stabilization	Entanglements and tie molecules	Delayed relaxation and creep resistance

Experimental Validation

The existence of a pseudo-vitrimeric state is therefore an experimental question. If delayed relaxation is controlled primarily by topology rather than exchange, the two mechanisms should differ in their temperature dependence, complex-viscosity response, creep recovery, and frequency-dependent viscoelastic behavior. An exchange-dominated vitrimer may show an Arrhenius-like temperature dependence over the temperature range in which bond exchange controls relaxation, whereas a topology-stabilized system may retain signatures associated with segmental relaxation or reptation. These trends are useful diagnostics, but neither temperature dependence alone is sufficient to establish the underlying mechanism [9,16].

Van Gurp-Palmen plots were built to characterize long-chain branching in polyolefin melts and are sensitive to branching architecture largely independent of molecular weight and temperature [28]. Cole-Cole representations offer a complementary check: the trajectory of loss modulus against storage modulus tracks changes in network structure [45]. Stress-relaxation tests, creep measurements, and broad-frequency oscillatory rheology round out the toolkit, and nonlinear extensional rheology adds a probe of strain hardening tied to long-chain branching that does not depend on chemistry at all [27,36]. None of these measurements is decisive alone; distinguishing topology-controlled relaxation from exchange-driven relaxation needs converging evidence from several techniques together. Chemistry, processing, molecular architecture, topology, and morphology should therefore be considered as interacting contributors to structural stability in semicrystalline polyolefins rather than assuming that long-term rheological performance is controlled by chemistry alone. Figure 8 summarizes this stabilization spectrum.

The Network-Stabilization Spectrum: From Thermoplastic to Thermoset

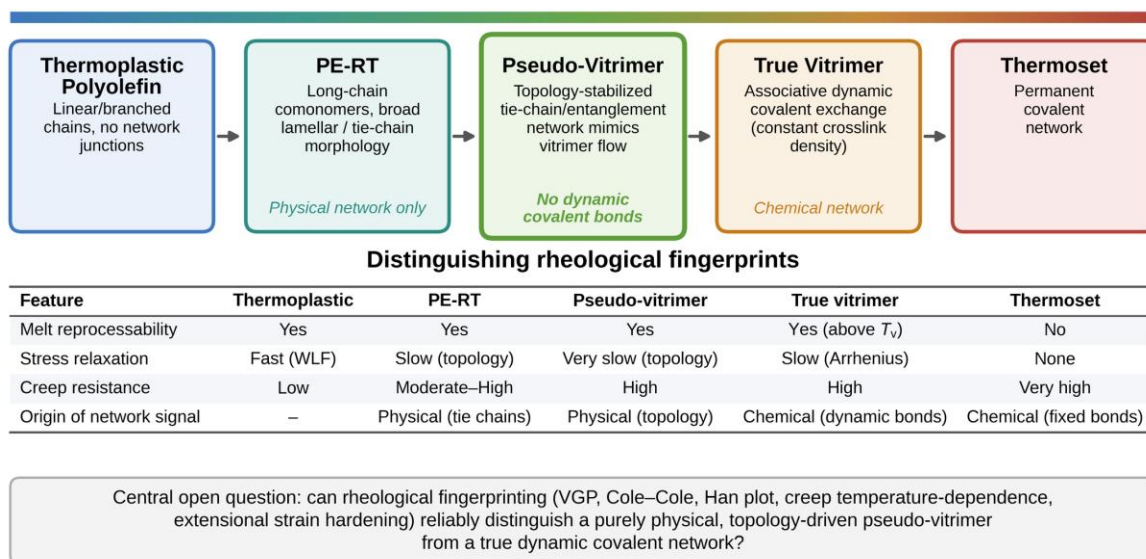


Figure 8. The network-stabilization spectrum from thermoplastic to thermoset, together with the rheological fingerprints proposed to distinguish each stage, including the position of the pseudo-vitrimeric state between conventional long-chain-branched polyethylene and a true dynamic covalent vitrimer.

CONCLUSIONS AND FUTURE PERSPECTIVES

A. What is established

Since the introduction of vitrimer networks, dynamic covalent chemistry has been investigated extensively as a route to combine network stability with reprocessability. Vitrimers demonstrated that structural integrity and melt reprocessability could coexist within the same material, challenging the traditional distinction between thermoplastics and thermosets and motivating research across a wide range of polymer systems.

In semicrystalline polyolefins, long-term rheological behavior appears to result from the interaction of molecular architecture, reactive processing, crystallization, and morphology rather than from any single structural feature. These factors influence stress transfer and relaxation over the material's service life, while dynamic covalent exchange remains one established route to rheological stabilization.

B. What remains unresolved

The pseudo-vitrimeric state proposed in this review should currently be regarded as a testable hypothesis, not an established material classification. The main unresolved issue is the absence of experimental criteria that can separate topology-controlled relaxation from relaxation governed by dynamic covalent exchange. Rheological data alone will not settle this, since similar responses can come from different molecular mechanisms; structural characterization has to accompany rheological measurement throughout.

The problem is particularly pronounced in semicrystalline polyethylene, where long-chain branching, tie-molecule density, crystallinity, molecular-weight distribution, catalyst residues, and processing history can change simultaneously during reactive processing. Model systems in which individual structural variables are controlled independently would provide a stronger basis for separating these contributions than studies based only on commercial materials.

C. What should be tested

Progress will require rheological measurements to be combined with structural characterization rather than treated as separate lines of investigation. SAXS, WAXD, electron microscopy, spectroscopy, molecular simulation, and time-resolved rheology can help establish relationships between molecular architecture and relaxation behavior. Predictive models that incorporate branching architecture, tie molecules, constrained amorphous regions, and semicrystalline morphology remain limited, which is an important obstacle to direct testing of the pseudo-vitrimeric hypothesis.

If topology engineering reproduces even part of the rheological advantages usually attributed to dynamic covalent networks, it opens additional routes to recyclable pressure pipes, structural polyolefins, and durable engineering plastics. Vitrimer chemistry itself keeps developing in parallel, through catalyst-free radical processing of polyethylene, dynamic compatibilization of mixed polyolefin waste streams, scalable vitrimer synthesis, and recyclable encapsulation materials for photovoltaic modules [46-50]. On the evidence reviewed here, chemical and topological approaches are best viewed as complementary strategies, with their relative importance set by the requirements of each application.

Whether the term "pseudo-vitrimeric state" is adopted more widely is secondary to the underlying question: how these structural factors jointly determine macroscopic behavior in semicrystalline polymers. Answering it will require the controlled model systems and combined structural-rheological characterization outlined above.

REFERENCES

1. Denissen W, Winne JM, Du Prez FE (2016) Vitrimers: permanent organic networks with glass-like fluidity. *Chem Sci* 7: 30-38 [\[CrossRef\]](#)
2. Winne JM, Leibler L, Du Prez FE (2019) Dynamic covalent chemistry in polymer networks: a mechanistic perspective. *Polym Chem* 10: 6091-6108 [\[CrossRef\]](#)
3. Montarnal D, Capelot M, Tournilhac F, Leibler L (2011) Silica-like malleable materials from permanent organic networks. *Science* 334: 965-968 [\[CrossRef\]](#)
4. Van Zee NJ, Nicolaÿ R (2020) Vitrimers: Permanently crosslinked polymers with dynamic network topology. *Prog Polym Sci* 104: 101233 [\[CrossRef\]](#)
5. Röttger M, Domenech T, van der Weegen R, Breuillac A, Nicolaÿ R, Leibler L (2017) High-performance vitrimers from commodity thermoplastics through dioxaborolane metathesis. *Science* 356: 62-65 [\[CrossRef\]](#)
6. E.K. Neidhart, M. Hua, Z. Peng, L.T. Kearney, V. Bhat, F. Vashahi, E.J. Alexanian, S.S. Sheiko, C. Wang, B.A. Helms, F.A. Leibfarth, C-H functionalization of polyolefins to access reprocessable polyolefin thermosets, *J Am Chem Soc* 145 (2023) 27450–27458 [\[CrossRef\]](#)
7. Kar GP, Saed MO, Terentjev EM (2020) Scalable upcycling of thermoplastic polyolefins into vitrimers through transesterification. *J Mater Chem A* 8: 24137–24147 [\[CrossRef\]](#)
8. Ricarte RG, Tournilhac, F, Leibler, L (2019) Phase separation and self-assembly in vitrimers: Hierarchical morphology of molten and semicrystalline polyethylene/dioxaborolane maleimide systems. *Macromolecules* 52: 432-443 [\[CrossRef\]](#)
9. Ricarte RG, Tournilhac F, Cloître M, Leibler L (2020) Linear viscoelasticity and flow of self-assembled vitrimers: The case of a polyethylene/dioxaborolane system. *Macromolecules* 53: 1852-1866 [\[CrossRef\]](#)
10. Zheng N, Xu Y, Zhao Q, Xie T (2021) Dynamic covalent polymer networks: A molecular platform for designing functions beyond chemical recycling and self-healing. *Chem Rev* 121: 1716-1745 [\[CrossRef\]](#)
11. Capelot M, Montarnal D, Tournilhac F, Leibler L (2012) Metal-catalyzed transesterification for healing and assembling of thermosets. *J Am Chem Soc* 134: 7664-7667 [\[CrossRef\]](#)
12. Ahmadi M, Hanifpour A, Ghiassinejad S, van Ruymbek E (2022) Polyolefins vitrimers: design principles and applications. *Chem Mater* 34: 10249-10271 [\[CrossRef\]](#)
13. Denissen W, Rivero G, Nicolaÿ R, Leibler L, Winne JM, Du Prez FE (2015) Vinylogous urethane vitrimers. *Adv Funct Mater* 25: 2451-2457 [\[CrossRef\]](#)
14. Stukenbroeker T, Wang W, Winne JM, Du Prez FE, Nicolaÿ R, Leibler L (2017) Polydimethylsiloxane quenchable vitrimers. *Polym Chem* 8: 6590-6593 [\[CrossRef\]](#)
15. Odenwald L, Wimmer FP, Mast NK, Schußmann MG, Wilhelm M, Mecking S (2022) Molecularly defined polyolefin vitrimers from catalytic insertion polymerization. *J Am Chem Soc* 144: 13226–13233 [\[CrossRef\]](#)
16. R.G. Ricarte, D.J. Shanbhag, Unentangled vitrimer melts: interplay between chain relaxation and cross-link exchange controls linear rheology, *Macromolecules* 54 (2021) 3304-3320 [\[CrossRef\]](#)
17. Wu SL, Yang HH, Chen Q (2024) Linear viscoelasticity of ABA-type vitrimer based on dioxaborolane metathesis. *Chin J Polym Sci* 42 (2024) 1495–1504 [\[CrossRef\]](#)
18. Hayashi M, Ricarte RG (2025) Towards the next development of vitrimers: Recent key topics for the practical application and understanding of the fundamental physics. *Prog Polym Sci* 158 (2025) 102026 [\[CrossRef\]](#)
19. Hayashi M, Ricarte RG (2025) Towards the next development of vitrimers: Recent key topics for the practical application and understanding of the fundamental physics. *Progr Polym Sci* 170: 102026 [\[CrossRef\]](#)

20. Clarke RW, Sandmeier T, Franklin KA, Reich D, Zhang X, Vengallur N, Patra TK, Tannenbaum RJ, Adhikari S, Kumar SK, Rovis T, Chen EY (2023) Dynamic crosslinking compatibilizes immiscible mixed plastics. *Nature* 616: 731-739 [\[CrossRef\]](#)
21. Maaz M, Riba-Bremerch A, Guibert C, Van Zee NJ, Nicolaÿ R (2021) Synthesis of polyethylene vitrimers in a single step: Consequences of graft structure, reactive extrusion conditions, and processing aids. *Macromolecules* 54: 2213-2225 [\[CrossRef\]](#)
22. Ezugwu EP, Lopez E, Ortin A, Bhattacharya M, Mantell SC. Relationship between microstructure changes and embrittlement during chemo-oxidative degradation of bimodal HDPE with short chain branches. *Polymer* 15; 313: 127752 [\[CrossRef\]](#)
23. Valdez S, Qiang Z (2025) Catalyst influence on the crystallization behaviors and mechanical properties of polyethylene vitrimers. *Macromolecules* 58: 11803-11815 [\[CrossRef\]](#)
24. Valdez S, Qiang Z (2025) Understanding non-isothermal crystallization behaviors of polyethylene-derived vitrimers. *Macromolecules* 58: 9348-9357 [\[CrossRef\]](#)
25. Fenimore LM, Chen B, Torkelson JM (2022) Simple upcycling of virgin and waste polyethylene into covalent adaptable networks: catalyst-free, radical-based reactive processing with dialkylamino disulfide bonds. *J Mater Chem A* 10: 24726-24745 [\[CrossRef\]](#)
26. Higuchi Y, Matsuba G (2024) Reversibility of semicrystalline polymers in creep testing by coarse-grained molecular dynamics simulations. *Macromol Chem Phys* 225: 2400076 [\[CrossRef\]](#)
27. Wagner MH, Bastian H, Hachmann P, Meissner J, Kurzbeck S, Münstedt H, Langouche F (2000) The strain-hardening behaviour of linear and long-chain-branched polyolefin melts in extensional flows. *Rheol Acta* 39: 97-109 [\[CrossRef\]](#)
28. Trinkle S, Walter P, Friedrich C (2002) Van Gurp-Palmen plot II - classification of long chain branched polymers by their topology. *Rheol Acta* 41: 103-113 [\[CrossRef\]](#)
29. Sun H, Vialon T, Guibert C, Casale S, Nicolaÿ R, Van Zee NJ (2025) Reactive processing of polyethylene with azidotriazine: From modified thermoplastics to injection moldable covalent adaptable networks. *ACS Appl Polym Mater* 7: 2123-2133 [\[CrossRef\]](#)
30. Manteghi A, Ahmadi S, Arabi H (2016) Polyolefin elastomer grafted unsaturated hindered phenol esters: synthesis and antioxidant behavior. *Des Monomer Polym* 19: 569-576 [\[CrossRef\]](#)
31. Mousavi-Fakhrabadi SH, Ahmadi S, Arabi H (2022) Mixing of hindered amine-grafted polyolefin elastomers with LDPE to enhance its long-term weathering and photo-stability. *Polym Degrad Stabil* 198: 109882 [\[CrossRef\]](#)
32. Salmani F, Shemshadi R, Moghaddampour IM, Ahmadi S, Naderi G, Sahraeian R, Paran SMR (2024) Mechanical, rheological, and heat seal properties of 1-octene grafted low density polyethylene films. *Macromol React Eng* 18: 2300060 [\[CrossRef\]](#)
33. Jahani Y, Farahani M, Arabi H, Ahmadjo S (2015) The influence of copolymerization condition on rheology, morphology and thermal behavior of polypropylene heterophasic copolymers. *J Macromol Sci A* 52: 532-539 [\[CrossRef\]](#)
34. Huang YW, Suazo MJ, Barbon SM, Brown HA, Auyeung E, Li Pi Shan C, Torkelson JM (2025) Propylene-ethylene copolymer covalent adaptable networks synthesized by resonance-stabilized, radical-based reactive processing with excellent elevated-temperature creep resistance. *ChemSusChem* 18: e202501137 [\[CrossRef\]](#)
35. Gao Y, Niu H (2024) Polypropylene-based transesterification covalent adaptable networks with internal catalysis. *Polym Chem* 15: 884-895 [\[CrossRef\]](#)
36. Dey I, Samanta K, Debnath T, Bose S (2026) Vitriimer-enabled circularity through upcycling mixed polyolefin waste from milk packets into valuable 3D printing feedstock. *Commun Sustain* 1: 50 [\[CrossRef\]](#)

37. Jahani Y, Ghetmiri M, Vaseghi MR (2015) The effects of long chain branching of polypropylene and chain extension of poly(ethylene terephthalate) on the thermal behavior, rheology and morphology of their blends. *RSC Adv* 5: 21620-21628 [\[CrossRef\]](#)
38. Dolatshah S, Ahmadi S, Ershad Langroodi A, Alavi A (2022) Long-chain branching of polyethylene terephthalate: Rheological/thermal properties of polyethylene terephthalate/carbon nanotube nanocomposite. *Polym Eng Sci* 62: 2322-2334 [\[CrossRef\]](#)
39. Jozaghkar MR, Jahani Y, Arabi H, Ziaee F (2018) Preparation and assessment of phase morphology, Rheological properties, and thermal behavior of low-density polyethylene/polyhexene-1 blends. *Polym-Plast Technol Eng* 57: 757-765 [\[CrossRef\]](#)
40. Jozaghkar MR, Jahani Y, Arabi H, Ziaee F (2019) Effect of polyethylene molecular architecture on the dynamic viscoelastic behavior of polyethylene/polyhexene-1 blends and its correlation with morphology. *Polym-Plast Technol Mater* 58: 560-572 [\[CrossRef\]](#)
41. Fenimore LM, Chen B, Chen Y, Barbon SM, Brown HA, Auyeung E, Li Pi Shan C, Torkelson JM (2024) Covalent adaptable networks and thermosets of multi-block ethylene/1-octene copolymers made by free-radical processing: Effects of melt flow index and crystallinity on thermomechanical properties and reprocessability. *Eur Polym J* 202: 112661 [\[CrossRef\]](#)
42. Suazo MJ, Fenimore LM, Barbon SM, Brown H, Auyeung E, Cespedes G, Li Pi Shan C, Torkelson JM (2024) Extrudable and highly creep-resistant covalent adaptable networks made from polyethylene and ethylene/1-octene copolymers by reactive processing with aromatic disulfide cross-links. *ACS Appl Polym Mater* 6: 14772–14783 [\[CrossRef\]](#)
43. Kim KJ, Ok YS, Kim BK (1992) Crosslinking of polyethylene with peroxide and multifunctional monomers during extrusion. *Eur Polym J* 28: 1487-1491 [\[CrossRef\]](#)
44. Zhao H, Duan P, Li Z, Chen Q, Yue T, Zhang L, Ganesan V, Liu J (2023) Unveiling the multiscale dynamics of polymer vitrimers via molecular dynamics simulations. *Macromolecules* 56: 9336-9349 [\[CrossRef\]](#)
45. Rolere S, Cartault M, Sainte-Beuve J, Bonfils F (2017) A rheological method exploiting Cole-Cole plot allows gel quantification in Natural Rubber. *Polym Test* 61: 378-385 [\[CrossRef\]](#)
46. Liu J, Wei W, Wang D (2025) Efficient compatibilization and toughening of polyethylene and polypropylene blends through dynamic cross-linking: A sustainable approach to polyolefin recycling. *ACS Appl Polym Mater* 7: 13777-13787 [\[CrossRef\]](#)
47. Ash S, Sharma R, Rabnawaz M (2024) Comparative study of polyethylene, Polypropylene, polyolefins silyl ether-based vitrimers. *Ind Eng Chem Res* 63: 22287-22297 [\[CrossRef\]](#)
48. Wang Z, Liu Y, Pang W, Chen A, Chen M (2024) Polyolefin vitrimers bearing acetoacetate functionality. *Sci Chin Chem* 67: 3861-3867 [\[CrossRef\]](#)
49. Ash S, Sharma R, Shaker M, Patil S, Cheng S, Rabnawaz M (2024) One-pot synthesis of robust silyl ether-based HDPE vitrimers with enhanced performance and recyclability. *Polymer* 308: 127374 [\[CrossRef\]](#)
50. Brastel A, Landa M, Ast J, Béjat T, Piluso P (2025) Transparent siloxane-based polyolefin vitrimer and Its use As an encapsulant for recyclable photovoltaic modules. *ACS Appl Polym Mater* 7: 10003-10015 [\[CrossRef\]](#)