

REPORT

POLYMERS

High-performance vitrimers from commodity thermoplastics through dioxaborolane metathesis

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Windmills, cars, and dental restoration demand polymer materials and composites that are easy to process, assemble, and recycle while exhibiting outstanding mechanical, thermal, and chemical resistance. Vitrimers, which are polymer networks able to shuffle chemical bonds through exchange reactions, could address these demands if they were prepared from existing plastics and processed with fast production rates and current equipment. We report the metathesis of dioxaborolanes, which is rapid and thermally robust, and use it to prepare vitrimers from polymers as different as poly(methyl methacrylate), polystyrene, and high-density polyethylene that, although permanently cross-linked, can be processed multiple times by means of extrusion or injection molding. They show superior chemical resistance and dimensional stability and can be efficiently assembled. The strategy is applicable to polymers with backbones made of carbon-carbon single bonds.

Thermoplastics are light, tough, and easy to process but are limited by their lower strength, structural stability at high temperature, abrasion, and solvent resistances. Cross-linking could be the solution to improve these properties but reduces the ability of thermoplastics to flow when heated. As a result, the synthesis, processing, and recycling of cross-linked polymers, called thermosets, are complex and costly, if not impossible. Environmental awareness and industrial competitiveness cripple the introduction and development of cross-linked polymer materials.

Vitrimers (1, 2) behave like permanently cross-linked materials at service temperatures, are insoluble at all temperatures, but can still flow when

heated. Vitrimers consist of a polymer network that is able to change its topology without decreasing its connectivity thanks to exchange reactions, which maintain constant the number of chemical bonds and cross-links. At high temperatures, exchanges are fast, and the material can be processed. By cooling, the shape is fixed either by quenching the exchange reaction (1, 2) or the motion of polymer molecules through glass transition (T_g) or crystallization (1, 3–5). Thus, vitrimers can be reshaped and recycled at will, while still exhibiting the desired chemical and mechanical resistance of cross-linked polymers. The first generation of vitrimers has demonstrated a great potential to bring malleability (1, 3, 4, 7), shape memory (8–10), and weldability (11, 12) to

classical epoxy and urethane thermoset resins (4, 7, 10, 13), composites (12, 14), and liquid crystalline networks (8, 15).

To expand their potential, vitrimers have to address two challenges. First, the vitrimer concept has to be applied to polymers with backbones solely made of carbon-carbon single bonds. Such polymers represent more than 75% of the 320 million tons of plastics produced each year. Secondly, the chemistry of vitrimers has to make them processable like thermoplastics, with the need to change neither the equipment nor the mass production speed currently used.

These two technological demands are scientific challenges that can be met by a different exchange reaction. Rapid exchanges can be obtained with a number of known reactions (16), such as transesterification of esters and boronic esters (17–19), olefin metathesis (20), transamination reactions (4, 21), thiol-disulfide exchange (22), degenerative chain transfer reactions (23, 24), or transalkylation (25). However, the chemical entities involved in these reactions are either not thermally or oxidatively stable or yield side reactions that create permanent cross-links under the conditions used to process thermoplastics (5). For radical reactions (23, 24)—for example, inter-chain recombination reactions—a yield as low as a 10th of a percent can block an extruder (26). The exchange reaction should also be compatible with chemical functionalities present in the polymer.

We report the metathesis reaction of dioxaborolanes, which takes place without the addition of a catalyst at temperatures as low as 60°C. In dioxaborolane metathesis, molecules reversibly exchange fragments linked together by the strong B–O bonds of the boronic ester groups (Fig. 1, A and B). Dioxaborolane metathesis allowed us to synthesize vitrimers from polymers containing exclusively C–C bonds in their

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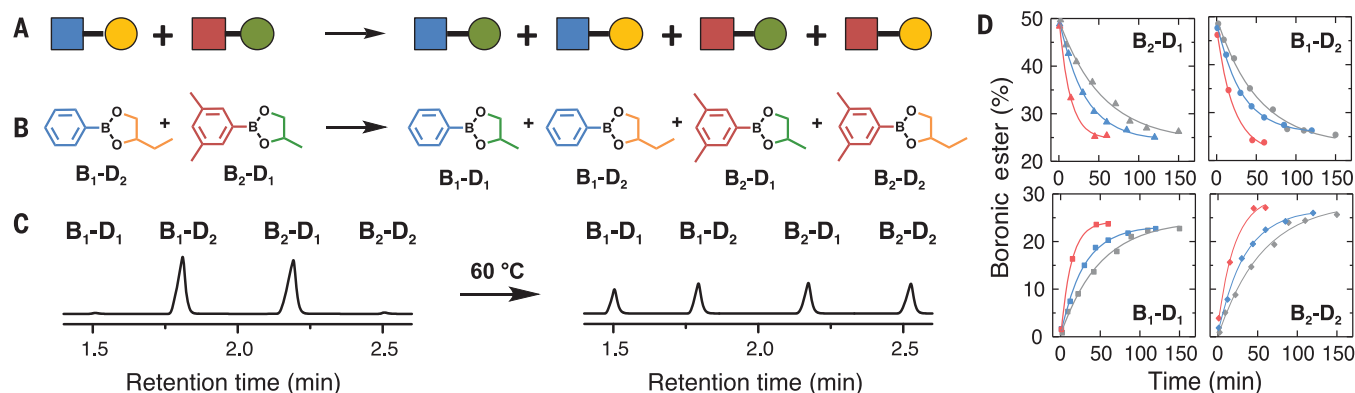


Fig. 1. Metathesis of dioxaborolanes. (A) General scheme of a metathesis reaction. (B) Metathesis of dioxaborolanes B₁-D₂ and B₂-D₁. (C) Gas chromatography traces of the reaction medium after 2 min (left) and 150 min (right) during metathesis of dioxaborolanes B₁-D₂ and B₂-D₁ in bulk at 60°C. (D) Consumption and formation of dioxaborolanes as a function of time for three reaction temperatures: gray, 60°C; blue, 85°C; and red, 150°C. Lines are drawn to guide the eye.

backbone with two methods: either by incorporating functional monomers during polymerization or by chemically modifying commercial polymers. We demonstrate the former method for poly(methyl methacrylate) (PMMA) and polystyrene (PS) and the latter for high-density polyethylene (HDPE), representative examples of widely used polymers.

Diols can undergo fast exchange reactions through transesterification with dioxaborolanes (17–19, 27). Dioxaborolanes are thermally stable and tolerant toward other functional groups (27, 28), but diols are not as tolerant. In methacrylates, for example, side reactions induced by diols yield permanent, nonexchangeable cross-links at high temperatures typical of polymer melt processing (table S1). In this context, we envisioned a possible exchange reaction between dioxaborolanes in the absence of detectable diol or water. We prepared two dioxaborolanes, B₁-D₂ and B₂-D₁, through the condensation of phenylboronic acid with 1,2-butanediol and 3,5-dimethylphenylboronic acid with 1,2-propanediol, respectively (figs. S1 and S2 and table S2). They were purified by means of sequential washing and subsequent distillation. Their purity was confirmed with gas chromatography, mass spectrometry, and ¹H and ¹³C nuclear magnetic resonance (NMR) spectroscopies (fig. S2). No remaining diols or phenylboronic acids or any other impurities could be detected with these techniques. To avoid a potential hydrolysis when studying exchange reactions, we used glassware that was flame-dried under a flow of dry argon (figs. S3 and S4). Surprisingly, when dioxaborolanes B₁-D₂ and B₂-D₁ were mixed at 60°C in the absence of solvent, the boronic esters B₁-D₁ and B₂-D₂ could be detected. After 160 min, the mixture contained an equimolar quantity of all four dioxaborolanes (Fig. 1, B to D). Neither free diol, water, nor phenylboronic acid could be detected in the reaction medium with gas chromatography or ¹H NMR spectroscopy (fig. S5). A metathesis reaction occurred. The kinetics of the exchange reaction was followed at different temperatures and could be well fitted with a simple second-order model, assuming a single metathesis rate (fig. S6). An activation energy of $\sim 15.9 \pm 0.5$ kJ/mol was found. As for mechanism, the metathesis reaction could occur through a direct process or through successive transesterifications of dioxaborolanes with undetectable traces of diols.

To generate vitrimers, we propose two complementary approaches: one based on the synthesis of copolymers containing pendant dioxaborolanes (Fig. 2A), the other on reactive processing of commercial thermoplastics (Fig. 2B). The metathesis reaction is used to both cross-link the polymers (Fig. 2C) and assure network topology fluctuations (fig. S7) and vitrimer behavior.

The first approach is exemplified for two of the most widely used polymers made from vinyl monomers, PMMA and PS. First, we prepared PMMA and PS copolymers carrying pendant dioxaborolane moieties by means of standard controlled radical copolymerization of MMA or styrene, with functional monomers containing a dioxaborolane or diol moiety (figs. S8 to S13). In the

latter case, the pending diol units were quantitatively transformed into dioxaborolanes through condensation with phenylboronic acid after polymerization. We achieved cross-linking using a bis-

dioxaborolane, either in solution or by reactive extrusion in the melt. All networks were insoluble in tetrahydrofuran, with insoluble fractions of $\sim 95\%$ (tables S3 to S7). Yet, they were

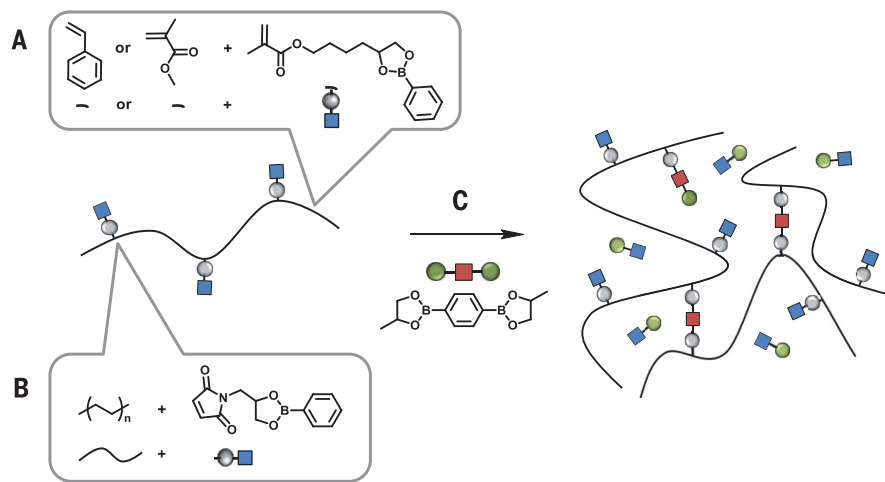


Fig. 2. Synthesis of vitrimers. (A) Synthesis of copolymers containing pendant dioxaborolanes from functional monomers. (B) Grafting of dioxaborolanes onto thermoplastic polymers by means of reactive processing. (C) Cross-linking of functional polymers containing pendant dioxaborolane units by means of metathesis with a bis-dioxaborolane. Free dioxaborolanes formed during the cross-linking process can be kept in the system as plasticizers or removed through evaporation.

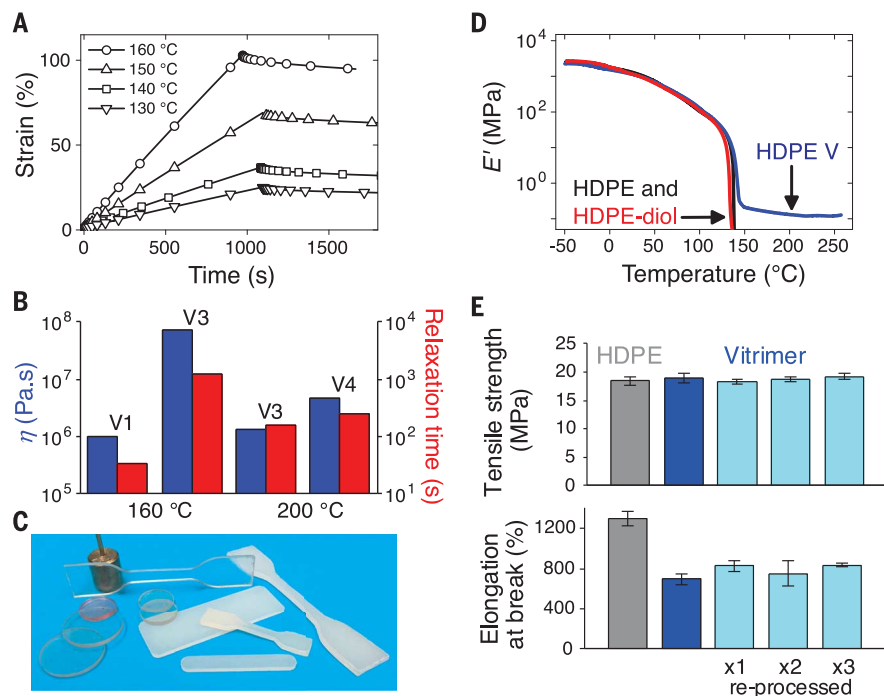


Fig. 3. Vitrimers from commodity polymers. (A) Step-stress creep of PMMA V1. (B) Viscosities (blue) and relaxation times (red) from creep (160°C) and frequency sweep (200°C) experiments for PMMA vitrimers with different structural parameters: mass average molar mass, functionality, and cross-linking density. V1, 26 kg/mol, 23 mol %, 2.2 weight % (wt %); V3, 120 kg/mol, 23 mol %, 2.2 wt %; V4, 100 kg/mol, 4 mol %, 2.2 wt %. (C) Injection- and compression-molded vitrimers. (Left) Injection-molded PMMA discs and dogbone samples (length, 6.6 cm). (Middle) Injection-molded PS discs. (Right) Compression-molded HDPE bars and dogbone sample. (D) Dynamic mechanical analysis of HDPE materials. (E) Tensile properties of HDPE (gray; $n = 5$ specimens tested), HDPE vitrimer (blue; $n = 4$ specimens tested), and recycled HDPE vitrimer (light blue; $n = 4$ specimens tested).

all able to flow when heated, as evidenced from step-stress creep experiments (Fig. 3A and figs. S14 to S18). Rheological properties can be conveniently controlled by appropriate choice of molecular parameters: copolymers molecular weight, fraction of pending dioxaborolanes, and/or cross-links. For example, the viscosity of PMMA vitrimers made from low- and high-molecular-weight precursors at 160°C varied between 1×10^6 and 2×10^6 Pa s, and relaxation times varied between 35 and 1300 s (Fig. 3B and figs. S14, S16, and S19 to S21). The viscosity activation energy of 76.7 ± 5.5 kJ/mol (figs. S19 and S20) is rather high. As a result, at 200°C—a temperature typical for PMMA processing—the complex viscosity of vitrimers (at 0.02 rad/s), even those made from high molecular weight precursors, was as low as 1.3×10^6 and 4.8×10^6 Pa s, depending on the fraction of pending dioxaborolanes (Fig. 3B and figs. S22 to S25). These viscosities are comparable with those of commercial PMMA thermoplastic grades. For PS vitrimer, which exhibits a lower friction coefficient, such low viscosities can be obtained even at 150°C (fig. S18).

We were able to extrude or injection-mold vinyl vitrimers using a laboratory-scale injection machine. The barrel and mold temperatures were set to 200°C and 180°C, respectively. Using a pressure of 12 bars, the mold could be filled within 15 s, just like for commercial thermoplastics. The whole injection process, including water-cooling of the mold below the glass transition temperature, took ~3 min. PMMA and PS vitrimer samples were transparent and colorless (Fig.

3C). The T_g of vitrimers was slightly lower than that of conventional homopolymers. At room temperatures, their mechanical properties were comparable (figs. S26 to S28).

Reactive mixing offers an alternative route to prepare vitrimers directly from commercial thermoplastics. For example, we grafted maleimides bearing dioxaborolane functionalities onto HDPE. We achieved quantitative grafting after 8 min of mixing at 170°C in the presence of dicumyl peroxide (figs. S29 to S33). A bis-dioxaborolane cross-linker was added, and reactive extrusion was continued for 6 min. Although extrudable, all samples could not be dissolved in good solvents of HDPE, such as xylene and orthodichlorobenzene at 140°C [gel fraction of $31.7 \pm 3.2\%$ ($n = 3$ specimens tested)] (table S8). Transesterification with diols instead of metathesis did not allow the preparation of HDPE vitrimers. Dynamic mechanical analysis and solubility tests (Fig. 3D, figs. S34 and S35, and table S8) show that efficient cross-linking by means of transesterification was not possible because of phase separation induced by diols (fig. S36).

For HDPE, the vitrimer viscosity from stress relaxation experiment was $\sim 1.8 \times 10^6$ Pa s at 190°C, and the melt flow index (MFI, 190°C/10 kg) was 3.7 ± 0.1 g/10 min ($n = 10$ specimens tested) (fig. S37 and table S8), a value typical of HDPE thermoplastic grade used for extrusion-blowing. The crystallinity of the vitrimer was slightly lower than that of its commercial thermoplastic precursor, but the Young's moduli and tensile strength were comparable (Fig. 3E and figs. S38 to S40).

The elongation at break of the vitrimer was decreased, a feature characteristic of cross-linked materials. In comparison with their thermoplastic counterparts, the vitrimers showed an improved melt strength and dimensional stability at high temperature (Fig. 3D and figs. S41 and S42).

All vitrimers could be processed, ground, and reprocessed several times by means of extrusion or compression- or injection-molding, just like commercial thermoplastics. The ability of vitrimers to be processed and recycled multiple times confirms the robustness of the dioxaborolane group. The absence of permanent nondynamic cross-links has been confirmed through selective diolysis of the dioxaborolane cross-links (fig. S43 and tables S8 and S9).

A transparent plastic object—for example, made of PS—placed in contact with a cleaning agent containing alcohol commonly becomes white and fragile because of the formation of multiple cracks. This phenomenon, known as environmental stress cracking, limits the applications of thermoplastics (29). We performed a simple test to demonstrate the improved environmental stress cracking resistance of vitrimers as compared with thermoplastics (Fig. 4A). PS vitrimer samples were immersed in an ethanol/water solution (9/1 v/v) under load for 3 hours and then tested for three-point bending resistance. The samples did not break, even under a flexural stress of 30 MPa. In comparison, thermoplastic PS immersed for as short as 2 min broke under a stress of 26.8 MPa. Longer immersion time led to fracture under even lower stress (fig. S44). Dioxaborolane vitrimers also resist hydrolysis. For example, the water uptake of PMMA vitrimer, even with 20 mole % (mol %) of pending dioxaborolane, was 2%, a value comparable with that of neat PMMA (tables S10 to S12). Even after immersion in pure water for a period of 3 months, no visible chemical degradation could be observed with infrared and ^1H NMR spectroscopies (fig. S45).

As illustrated in Fig. 4B, exchangeable cross-links improve creep resistance even at high temperature—for example, at 80°C for 60,000 s under a constant load of 5 MPa for HDPE vitrimers with a melting temperature of 128°C, which are conditions relevant for above-mentioned applications.

Fields as different as packaging, electronics, robotics, or microfluidic devices benefit from assembling polymers with different properties. Yet, most polymers of different chemical nature cannot be welded because with rare exceptions, polymers are incompatible. For thermoplastics, various strategies using reactive or compatibilizing tie layers have been designed to alleviate this issue. For example, PMMA and PE were glued by using grafted copolymer compatibilizers. In a 180° peeling test, an adhesion strength of 400 N/m was obtained (30). Dioxaborolane vitrimers can be easily and efficiently welded without the need for a tie layer (fig. S46). First, the presence of pending polar dioxaborolanes brings some compatibility and adhesion, as demonstrated with adhesion tests on dioxaborolane-modified PE and PMMA thermoplastics (Fig. 4C and fig. S47). Second, in

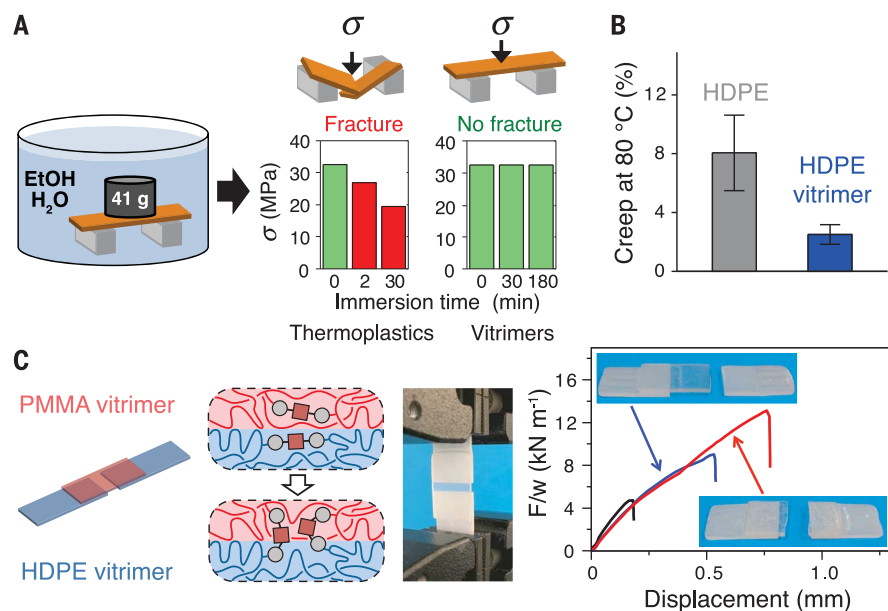


Fig. 4. Superior properties of vinyl and olefin vitrimers. (A) Enhanced environmental stress-cracking resistance of PS vitrimers by ramping the flexural stress after loading in a stress-cracking agent at room temperature. (B) Enhanced creep resistance at 80°C of HDPE vitrimer ($n = 4$ specimens tested) as compared with the commercial thermoplastic precursor ($n = 5$ specimens tested). (C) Enhanced adhesion of PMMA and HDPE vitrimers. Shown are a schematic representation, photo, and lap-shear testing of double lap joints of PMMA/HDPE dioxaborolane thermoplastic precursors (black, contact time 10 min, adhesive failure), and PMMA/HDPE vitrimers for two contact times, 10 min (blue, adhesive failure) and 20 min (red, bulk failure in PMMA).

vitrimers, exchange reactions can lead to the formation of covalent bridges across the interface and further enhance the adhesion. After 10 min of contact at 190°C under 11 kPa pressure, the adhesion strength of PE and PMMA vitrimers in lap-shear test was as high as $11,500 \pm 4500$ N/m ($n = 4$ specimens tested) (fig. S48). After welding for 20 min, the adhesion of vitrimers was so strong that bulk fracture in PMMA systematically occurred (fig. S49).

We found that dioxaborolanes undergo a rapid metathesis reaction at moderate temperatures without the need of a catalyst. Dioxaborolanes are thermally and chemically resistant and tolerant toward many functional groups. Simple dioxaborolane additives can change a commercial polymer with a C-C backbone into a vitrimer. We show that vitrimers exhibit improved melt strength, dimensional stability at elevated temperatures, and solvent and environmental stress-cracking resistance. In contrast to thermosets and vitrimers obtained with other cross-linking methods, dioxaborolane-based vitrimers are processable and recyclable just like thermoplastics. Starting from commercial monomers and polymers, a large range of vitrimer structures and properties can be attained by changing the molecular parameters of polymers and concentration of dioxaborolane additives. Dioxaborolane-based vitrimers bring possibilities of straightforward repair, assembly, and alloying of incompatible polymers and may be a route to the recycling of plastics without the need to sort them.

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SUPPLEMENTARY MATERIALS

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Materials and Methods
Figs. S1 to S49
Tables S1 to S12
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Editor's Summary

Processable cross-linked polymers

Thermoplastics can be made stiffer and more durable by crosslinking them, but this makes it more difficult to reprocess and recycle them. Röttger *et al.* show that the transesterification of boronic esters grafted onto common polymers such as polyethylene and polystyrene improves their shape stability and chemical resistance. However, unlike traditionally cross-linked materials, their polymers can still be extruded or injection-molded. This is because the covalent cross-links can undergo rapid exchange reactions, which allows the material to flow at high temperatures while still retaining a cross-linked structure.

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