

Polymeric materials for long-term durability of photovoltaic systems

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ABSTRACT: Photovoltaic (PV) technology has evolved rapidly in the past few decades and now encompasses a large variety of materials and device structures. A key aspect to be taken into account in any PV technology is the operational durability of the systems in outdoor conditions. Clearly, loss of performance during operation represents a significant drawback and limitation in the commercialization of this technology. In this context, the large compositional flexibility of polymeric materials as well as their proven easy processability may be of great help in imparting improved durability to PV systems. In this review, a summary on the state of the art and most recent developments in the field of polymeric materials for improved long-term durability of PV devices is presented, with particular emphasis on the use of polymers as encapsulation materials and protective coatings in the field of both PV and light-concentration systems. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43080.

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INTRODUCTION

Photovoltaic (PV) technology has evolved rapidly in the past few decades. Novel materials and device structures have fully entered the PV arena and are now working alongside other well-consolidated, commercially available technologies. To this end, in order to ensure the commercial viability of any PV technology, several aspects related to materials and devices need to be addressed simultaneously. In particular, in addition to maximizing the output power conversion efficiency (PCE), the processing costs of devices and modules need to be minimized so that PV systems may be cost-competitive against other conventional power-generation systems.¹ Furthermore, another key aspect that has gained increasing importance in the last few decades, both in conventional as well as in more recent emerging PV technologies, is the need to ensure the long-term operational durability of the systems in outdoor conditions. Clearly, loss of performance during operation represents a significant drawback and limitation in the commercialization of this technology. In this context, the large compositional flexibility of polymeric materials as well as their proven easy processability on a large scale may be of great help in imparting improved durability to PV systems. In recent years, the use of polymers for enhanced lifetime and durability in the PV field has increased dramatically, irrespective of the specific PV technology. Therefore, this is an area of great academic and industrial interest.

The aim of this review is to present a summary of the recent developments in the field of polymeric materials for long-term durability of PV systems. After a brief overview on consolidated and emerging PV technologies, the current state of the art and the most recent progress in the use of polymeric materials for improving the durability of PV systems will be analyzed. Aspects related to the photochemical and thermal stability of photoactive conjugated polymers will not be discussed in this review because a huge body of work is already available on this topic in the specialized literature.^{2–10} Instead, particular emphasis will be given to the use of polymers as encapsulation materials and protective coatings in the field of both PVs and light-concentration systems, with the ultimate aim of improving the durability of the materials and lengthening the operational lifetime of the working devices.

PV Technology

The PV market has experienced tremendous growth in the past few decades, mainly due to the unquestionable leading role played by crystalline silicon (Si)-based devices that have largely dominated the PV scene so far and have now reached PCEs in excess of 25% in single-junction, crystalline Si-based devices.¹¹ Despite the high efficiency that crystalline Si-based PVs can provide, this technology still presents some drawbacks related to its high material purity requirements, high material consumption, and high-energy-demand, low-throughput production processes.¹ In the attempt to overcome some of these

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limitations, other inorganic-based PV technologies have been developed, including (hydrogenated) amorphous silicon (aSi:H), cadmium telluride (CdTe), copper indium gallium diselenide [Cu(In,Ga)Se₂], and gallium arsenide (GaAs) PV cells. While some of these systems present some merits with respect to crystalline Si (e.g., reduced active layer thickness, reduced material consumption, mechanical flexibility), their widespread use is still strongly limited by some clear technological disadvantages that include the severe photoinstability of aSi:H¹² and existing concerns related to the potential toxicity, limited availability, and price volatility of some of the critical materials employed in the best-performing devices.^{13,14}

Alongside inorganic-based PV cells, organic, hybrid organic-inorganic, and polymeric materials have also been explored and developed in the past twenty years to be employed as active materials in different types of so-called third-generation PV technologies, some of which are about to see actual commercialization.^{15–17} Among these, dye-sensitized solar cells (DSSCs) exploit the use of solution-processable active materials to produce devices with a high freedom of design, color tunability, and PCE values exceeding 11–12%.^{18–21} Beside DSSCs, another relatively new class of organic-based PV devices that is fast approaching the market makes use of semiconducting conjugated polymers as photoactive p-type materials employed in conjunction with an n-type organic small molecule or polymer.^{22,23} These so-called bulk-heterojunction (BHJ) polymer solar cells (PSCs) have experienced enormous improvements in the past decade in terms of both materials and device engineering, recently leading to record PCE values in excess of 9–10% in lab-scale devices.^{11,24–26} In addition to device efficiency, great efforts have been addressed in the last few years to increasing their lifetime and developing cost-effective scalable manufacturing processes to shorten the lab-to-fab gap for this technology, and a few demonstrations have been presented of middle-to-large-scale device and module production.^{27–32}

Very recently, perovskite solar cells have also emerged as a truly disruptive technology that has demonstrated an impressive

growth in the last two to three years, with PCE values now approaching 20%.^{33,34} These systems are, however, still in their infancy, and several issues still need to be fully investigated before their actual widespread deployment, including their limited outdoor stability, their large-scale manufacturability and reproducibility still to be proven, and the critical toxicological profile of some of the components used in the best-performing device configurations.^{35–38}

Light-Concentration Systems

Alongside conventional and more advanced PV technologies such as those presented in the previous section, auxiliary systems to concentrate the incident solar light have also been developed in the past decades in the attempt to overcome some of the limitations encountered with high-efficiency PV cells and modules (namely, high production costs and limited availability or price volatility of some materials) and to further boost their performance. The basic idea behind the so-called concentrated photovoltaic (CPV) systems is the possibility to replace the expensive PV cell area with inexpensive optical components such as parabolic mirrors and Fresnel lenses to focus *direct* sunlight onto small-area high-efficiency PV cells.^{39–41} In this way, concentration factors as high as hundreds of suns can be achieved, thus resulting in improved PV performance, due to the increased illumination intensity experienced by the PV cells. However, these systems are not free from limitations that require specific technological precautions. First, the optical components must provide satisfactory performance over the entire service life of the PV modules, so the durability of the materials (typically polymeric) employed in their fabrication represents a key issue. In addition, very often cooling and sun-tracking systems are required to ensure optimal operation of the CPV ensemble.^{42–44}

An alternative light-concentration technology known since the late 1970s that has gained momentum and renewed interest in the past few years is the so-called luminescent solar concentrators (LSCs).^{45,46} LSCs consist of a transparent host matrix (typically polymeric) doped with one or more luminescent species.

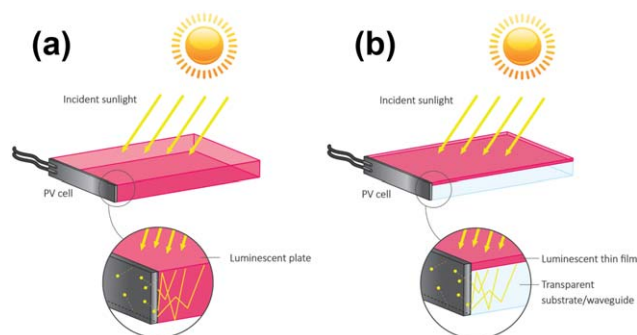


Figure 1. Schematic representation of the most common LSC configurations: (a) bulk and (b) thin film. In the bulk-plate configuration, a slab of transparent (typically polymeric) host matrix that also serves as the waveguide is lightly doped with one or more luminescent species. In the thin-film design, the waveguiding function is served by a transparent substrate (typically glass) onto which the doped polymeric carrier is deposited as a coating. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Upon sunlight exposure, the solar photons incident on the LSC are absorbed by the luminescent molecules and then re-emitted at a different (generally longer) wavelength. Given that the refractive index of the host matrix is higher than that of air, a fraction of re-emitted photons is confined within the polymer by total internal reflection and becomes concentrated along the edges of the plate, where it can be collected by small-area PV cells (Figure 1). By appropriate matching of the optical response of the luminophore with the solar emission spectrum and the band gap of the PV cell, PV device operation can be optimized and the cost of solar electricity can be reduced.⁴⁷ In addition, the light weight of the materials employed, the possibility to modulate their color and shape, and their ability to perform well also under diffuse light make LSC systems very attractive for building-integrated PV applications and for installation in the urban environment, where they may help overcome some of the limitations of traditional PV systems.⁴⁸ Due to the materials involved in their fabrication (in most cases organic and polymeric), the lifetime of LSC systems in outdoor operating conditions still represents one of the main challenges in this field, and in recent years strategies to improve the durability of materials and devices are being explored, as will be described in detail in the next section.

DURABILITY OF PV SYSTEMS AND THE ROLE OF POLYMERS

During outdoor operation, PV systems may be subjected to a combination of different external stresses (weather, soil, and so on) that will potentially affect their optical, mechanical, thermal, chemical, and photochemical stability and may eventually lead to a decrease in output performance. This loss of device or module efficiency represents a clear limitation that can hardly be overcome by simply relying on the intrinsic stability and quality of the single material constituting the photoactive element. In this context, the use of polymeric materials as encapsulants, superstrates, or protective coatings may allow increased durability to be imparted to the PV systems in a relatively

straightforward way. Thanks to their intrinsic light weight, their consolidated suitability for large-scale processing, and the possibility to synthetically tune their optical, chemical, and mechanical characteristics for a specific target application, polymers have been extensively employed in the PV field as encapsulants for conventional Si-based PV devices or as optical elements in CPV systems. More recently, the progress made in other relatively young PV technologies, such as those based on organic materials (DSSCs, PSCs, LSCs), has pushed further the use of polymeric materials for improved PV durability, with more stringent requirements mainly dictated by the more vulnerable photoactive materials involved. Within this framework, both consolidated and novel applications of polymers for the durability of PV systems will be discussed in the following paragraphs.

Polymeric Materials as Encapsulants

Encapsulation of Inorganic PV Cells. Polymeric materials are widely used as encapsulants in the manufacturing of inorganic (Si-based) PV modules. A simplified scheme of the position and roles of encapsulant films across a representative PV cell architecture is shown in Figure 2.

According to Czanderna *et al.*,⁵⁰ the encapsulant layer must fulfill some basic requirements:

- Provide structural support for PV cell fabrication, handling, installation, and operation.
- Achieve and maintain durable optical properties (at least 90% of light transmission and <5% loss of transmission after 20 years).
- Provide physical insulation of solar cells and circuits from degrading environmental factors like rain, dirt pickup, and salt spray.
- Achieve and maintain a reliable long-term electrical insulation of the circuit elements for safety reasons.

Since one of the major goals in all PV technologies is to generate electrical energy inexpensively, it is easily understood that relatively cheap polymeric materials, such as ethylene–vinyl acetate copolymers (EVA) and to a lesser extent poly(vinyl butyral) (PVB), were historically chosen as encapsulant materials, already since the early 1980s. It was, however, soon apparent that polymer degradation, especially polymer yellowing or discoloration,^{50,51} represented a major issue. Indeed, discoloration of EVA reduces the optical transmission, power output, and service life of PV modules and enhances the corrosion of metallic circuits.

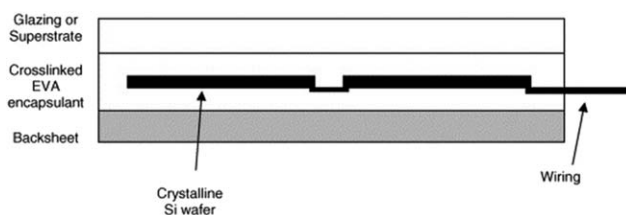
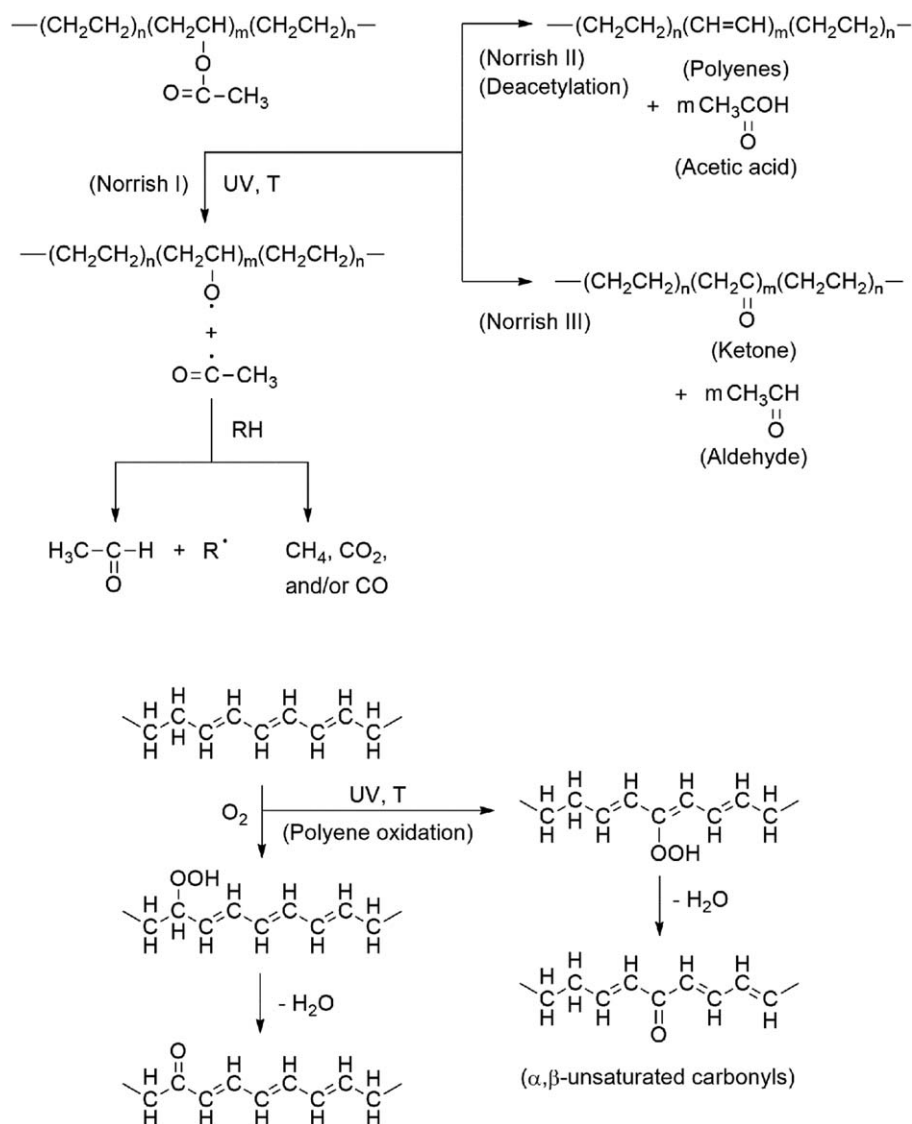


Figure 2. Schematic cross section of a typical Si-based PV module. Reproduced from ref. 49, with permission from Elsevier.



Scheme 1. Main degradation mechanisms of EVA induced by UV and temperature. Redrawn from ref. 50.

EVA is a random copolymer of ethylene and vinyl acetate. For PV applications, a grade with around 33% (by weight) of vinyl acetate is normally used. The thermal and photothermal degradation behavior of EVA has been extensively studied, and the main reaction pathway is schematized in Scheme 1. Photoinduced Norrish II reactions lead to the generation of acetic acid and polyenes, while the Norrish I reaction produces acetaldehyde and other gases. The main reason for EVA discoloration is likely the formation of polyenes and structures with α,β -unsaturated carbonyl groups. Moreover, the acetic acid byproduct shows an autocatalytic effect on EVA yellowing. To improve its outdoor durability, commercial-grade EVA films are formulated with curing agents, ultraviolet (UV) absorbers, and photoantioxidant and thermoantioxidant additives.⁵² In addition, crosslinking is needed to avoid or minimize creep during long-term exposure to relatively high temperatures. The crosslinking reaction is accomplished by peroxy-type initiators, and it is normally carried out at 160°C for 12–25 min. Crosslinking generates a gel content around 70% and prevents flow of the

polymer film when exposed to service temperatures, which can reach 70–80°C depending on the geographical location.^{53,54} The extent of EVA discoloration can be significantly reduced by formulation with stabilizing additives and by the use of UV-filtering glass or polymeric stable superstrates, which can remove the UV light fraction with $\lambda < 350$ nm.^{55,56} This is actually the current state of the art of front-sheet layers for conventional Si-based solar cells.

Because performing real-time natural weathering tests on solar cells for over 20 years is impractical, the implementation of suitable accelerated weathering tests is crucial. Pern *et al.* characterized changes in the optical and electrical properties of crystalline Si and aSi:H solar cells fabricated with different combinations of superstrate/EVA/substrate laminates and exposed to high-power (from 3 to 9 equivalent suns) simulated solar light at high temperature.⁵⁷ Both glass and high-stability semifluorinated thermoplastics [Tedlar poly(vinyl fluoride) (PVF) and Tefzel ethylene tetrafluoroethylene (ETFE) films] were considered as outer layers. An integrated, noninvasive

characterization protocol including UV–vis–IR spectroscopy was used. It was found that the discoloration rate of EVA films in the laminates is strongly affected by the weathering conditions. The yellow-to-brown discoloration patterns were attributed to the formation of C=C conjugation. Considering commercial EVA formulations, a rather fast loss of the UV-absorbing additive was reported, and faster peroxy-cure EVA laminates were found to be intrinsically more stable than the regular-cure grade. The same behavior was reported also by Agroui *et al.*,⁵² confirming the superior stability of fast-cure EVA grades. The determination of type and concentration of stabilisers present in encapsulation films is crucial for a correct assessment of the durability of polymers used as encapsulants or as front and back sheets in PV modules. To this end, suitable experimental protocols were described based on a direct analysis in real time coupled with mass-spectrometry-combining (GC–MS and HPLC–MS) techniques.⁵⁸

While glass is routinely used as a front-sheet lamination layer to protect the EVA encapsulant, different polymeric materials are used as an alternative to glass as back sheets. Actually, glass–plastic lamination offers several advantages: the fabrication process is faster and simpler, the module is lighter, and its installation easier. Back-sheet materials must provide mechanical robustness and a barrier to oxygen and moisture, whereas UV protection is in this case of minor importance. Several thermoplastics can be used, such as partially fluorinated polyolefins and polyesters. To further improve their barrier properties, a thin layer of aluminum, alumina, or silicon oxide by vapor phase deposition can be often coupled to polyester films. Oreski *et al.* exposed PVF, poly(vinylidene fluoride) (PVDF) (in a blend with acrylics), and polyethylene terephthalate (PET) films to “damp-heat tests,” consisting of an accelerated aging in an environment with 85% relative humidity and a temperature of 85°C.⁵⁹ They found significant hydrolysis of the polyester and extensive recrystallization of PVDF, which led to a loss of transparency and embrittlement. It was found that PVF shows the best damp-heat-test stability behavior with very limited formation of C=C unsaturation and no effect on mechanical properties. Hydrolysis and postcrystallization of PET were reported also by other authors.⁶⁰ PVF back-sheet films are intrinsically stable towards hydrolysis, making PVF a key polymer in commercial PV modules that have been in real-life service for about 25 years.

In a very recent work by Kim *et al.*, high-conductivity PVDF-based composite films were proposed for use as back sheets in PV applications.⁶¹ These systems consist of a single-layer PVDF structure containing varying amounts of aluminum nitride and boron nitride filler particles that were purposely surface modified with silane coupling agents to improve their compatibility with the polymeric matrix. The addition of such inorganic particles was found to significantly improve the thermal conductivity of bare PVDF and yielded increased mechanical properties as well as significantly reduced moisture swelling of the polymeric film. These properties make such a PVDF-based composite a promising long-lasting alternative to conventional PET-based back sheets.

In addition to halogenated polymers such as PVF and PVDF, examples of halogen-free systems have been proposed as back-sheet material alternatives to PET, some of which have also reached successful commercialization.^{62,63}

Recently, the durability of PVF and PET back-sheet materials was studied in an attempt to correlate actual degradation in fielded modules with results obtained from accelerated testing protocols.⁶⁴ The results of this study showed that the real-life behavior is better predicted by a combination of UV irradiation, temperature, and moisture exposure than by the damp-heat test alone. Moreover, exposure to more than 1000 h of a damp-heat test produces polymer failure mechanisms that may not be observed in the field, including yellowing.⁶⁵ However, the yellowing of back sheets is reported to have only a minor effect on PV electrical performance.⁶⁰ The worst modes of failure in this respect are represented by cracks and delamination, which negatively affect barrier properties.⁶⁶

Despite the higher stress level imparted to back-sheet materials when subjected to prolonged artificial weathering like the damp-heat test compared with outdoor field exposure, accelerated indoor tests represent a valuable tool to investigate the effect of back-sheet material degradation on the functional response of the PV modules. In particular, in a recent work by Voronko *et al.*, six different types of multilayer polymeric back sheets were damp-heat tested for 2000 h, and the chemical and physical modifications occurring to the materials upon aging were examined in relation to PV module performance loss.⁶⁷ It was shown that the absolute values of water vapor transmission rate and oxygen transmission rate of the pristine back-sheet materials do not directly correlate with the observed PV module performance loss in damp-heat tests. Conversely, strong deviations in the aging-induced changes in the WVTR and OTR (positive or negative) were found to be associated with power output loss upon aging.⁶⁷ A similar approach based on the evaluation of material modifications during artificial weathering and the relative correlation with module performance was presented in an earlier work,⁶⁸ where both UV exposure and prolonged (3000 h) damp-heat tests were employed on Si-based modules with different types of multilayer back-sheet materials [Tedlar/PET/Tedlar (TPT) and Tedlar/PET/EVA (TPE)]. It was found that the type of back-sheet material did not affect significantly the module performance upon weathering. Instead, a major contribution to power loss was shown to be caused by the chemical degradation (hydrolysis) of EVA and PET, and the release of free acetic acid from EVA was correlated with the power loss of the PV modules. In particular, the hydrolysis of PET during damp-heat tests was reported by other authors to be inversely proportional to the concentration of chain-end groups in the pristine unaged material, which results in an autocatalyzed reaction whose rate increases as the reaction proceeds.⁶⁹ As a result, a reliable prediction of the lifetime of PET-based back sheets was shown to be possible only for damp-heat tests of at least 2500 h, so as to avoid underestimation of the degradation kinetics of PET at longer exposure times.

A search for alternatives to glass/EVA laminates for the integration of c-Si PV modules in powered boats was also reported.⁷⁰

A material selection exercise was described that included 15 different polymers as front-sheet and back-sheet materials, including epoxies, ETFE, poly(tetrafluoroethylene) (PTFE), polypropylene, polyethylene, polyimides, PVB, and others. The selection criteria were, however, mostly focused on weight and cost, with underestimation of outdoor durability behavior.

Another alternative to glass may be represented by polymeric front sheets with integration of thin inorganic barrier layers. Rossi *et al.* described the chemisorption of self-assembled monolayers of perfluoroalkylsilanes on commercial barrier foils consisting of PET-SiO_x (12 μm) and ETFE-SiO_x (100 μm).^{71,72} Different types of environmental degradation factors were simulated, including acid rains and damp heat. The surface showed a durable hydrophobic behavior (contact angle against water about 130°), suggesting a potential use as an easy-cleaning PV coating.

With the similar aim of imparting easy cleaning functionalities, a moth-eye biomimetic, superhydrophobic, and self-cleaning protective film for PV cells was fabricated by a combination of hot embossing and UV-nanoimprint lithography onto PET foils.⁷³ Nanostructuring of the surface was achieved by direct hot embossing of a fluororesin deposited onto PET (structure of fluororesin undisclosed) and by nanoimprint lithography of a UV-curable silicone resin. A real superhydrophobic behavior with contact angle against water of >150° was reported. Nanostructure formation also led to the suppression of the reflection of incident light. The PV efficiency of a c-Si solar cell coated with the superhydrophobic and antireflective films was shown to increase by up to 2.08%.

Another key factor to be taken into account in order to maintain high solar cell efficiency and to prevent polymer thermal degradation is heat management and dissipation. Hence, packaging materials for PV modules should possess good thermal conductivity.^{74,75} PVDF-based composites containing silane-modified aluminum nitride and boron nitride fillers were described and proposed as high-thermal-conductivity back-sheet films.⁶¹ Similarly, polymer nanocomposites based on vinyl chloride-acrylonitrile copolymers and boron nitride nanotubes were described and proposed as highly transparent (transmittance 93% over the whole visible range) barrier films,⁷⁶ but no durability data or examples of application onto working PV cells were reported.

Encapsulation of Organic PV Cells. In the area of organic-based PVs, PSCs promise to offer several advantages over the more mature Si-based PV technologies, mainly due to the possibility to employ continuous high-throughput roll-to-roll techniques for their fabrication, thus resulting in prospective lower production costs. Due to the intrinsically limited stability of the materials employed (conjugated semiconducting polymers), the prolonged outdoor stability of PSC systems still represents a critical issue in the commercialization of this technology. The main reasons for PSC degradation when exposed to the outdoor environment have been extensively investigated⁹ and mainly concern breaking of π -conjugation due to light-activated reaction of oxygen with polyene systems, polymer chain photolysis activated by residual metal catalysts, and oxidation and delamination of low-work-function metal electrodes in the pres-

Table I. Specifications and Requirements of Encapsulating Materials for Organic PV Cells

Encapsulating material property	Specifications and requirements
WVTR	10^{-4} – 10^{-6} g m ⁻² day ⁻¹
OTR	10^{-3} – 10^{-5} cm ³ m ⁻² day ⁻¹
T_g	-40°C
Light transmission from 400 nm to 1100 nm	>90%
Hydrolysis	None at 80°C, 100% RH
Water absorption	<0.5% at 20°C, 100% RH
Thermal oxidation	Stable up to 85°C
Mechanical creep	None at 90°C
Elastic modulus	<20.7 MPa at 25°C
Chemical resistance	Inert with Cu at 90°C
UV-induced degradation	None for $\lambda > 350$ nm
Hazing	None at 80°C, 100% RH

Adapted from ref. 50.

ence of oxygen and moisture.⁵ Therefore, the durability and lifetime of PSC devices will depend on the intrinsic stability of photoactive materials, device interfaces, and substrate and barrier layers. The development of high-performance encapsulation materials is therefore crucial to the commercial success of this technology. To this end, optimal encapsulation materials should offer low permeation to oxygen and water, intrinsic UV stability and filtering of high-frequency solar photons, strong adhesion to the solar cell, and high transparency in the visible range.

An area where extensive studies on outdoor durability have been carried out and from which the PSC technology can profit is that of organic light-emitting diodes (OLEDs), which suffer from similar durability problems and have already gained extensive industrial success.⁷⁷ The practical use of OLEDs requires encapsulation of the device with high-barrier packaging materials, characterized by excellent light transmittance in the whole visible range and with a water vapor transmission rate (WVTR) and oxygen transmission rate (OTR) of the order of 10^{-6} g m⁻² day⁻¹ and 10^{-3} g m⁻² day⁻¹, respectively.⁷⁸ Such values cannot be reached by conventional polymeric packaging materials, and therefore more complex polymeric/inorganic multilayer flexible structures must be considered. The idea to achieve ultrabARRIER properties by alternating inorganic and organic layers is based on the concept of decoupling the defects (pinholes) present in the thin inorganic layer and on the realization of a tortuous path for the gas/vapor molecules. However, recent studies suggest that a medium barrier material with a WVTR as low as 10^{-3} g m⁻² day⁻¹ could be enough to protect PSC devices.^{79,80} The general requirements and desired properties for flexible PSC packaging materials are summarized in Table I.

Materials and methods for an efficient encapsulation of PSC devices were recently reviewed.⁸¹ Among polymeric materials, the use of EVA, ethylene methylacrylate (EMA) copolymers, PVB, thermoplastic polyurethanes, and cyclized amorphous

perfluoropolymers (Cytop) was discussed,⁸¹ mainly based on an examination of patent literature or commercial data sheets.

Dennler *et al.* reported on the first shelf-lifetime study of a conjugated polymer–fullerene solar cell encapsulated with flexible and transparent polyethylene naphthalate (PEN) films coated with high barrier layers of SiO_x and organosilicon grown sequentially and deposited by plasma-enhanced chemical vapor deposition (PECVD).⁸² It was shown that the encapsulated PSC devices retained more than 50% of their initial efficiency when stored in the dark for 3000 h, whereas the same PSC device simply laminated with a polyester film has a shelf life of less than 200 h.

Poly(vinyl alcohol) (PVA) can be considered a promising candidate for the development of multilayer encapsulating foils for PSC because of its excellent barrier properties toward oxygen permeation.⁸³ The stability of PVA films when exposed to combined photo- and thermal aging cycles was deeply investigated, combining irradiation to light with $\lambda > 300$ nm and thermal oxidation at 60°C.⁸⁴ It was found that PVA is stable to thermo-oxidation even after 7000 h heating. Photo-oxidation, however, causes a progressive decrease of polymer transmittance. Degradation products from PVA photo-oxidation are typically constituted by carboxylic acids and low-molecular-weight volatile fragments like acetic, oxalic, and malonic acids. Photo-oxidation mainly involves the top 5- μm -thick layer of the material. However, PVA appears to be rather stable to photoinduced degradation in the absence of oxygen, suggesting a potential use as an inner layer in a multilayer packaging film for PSCs. The same authors also described the use of PVA–clay nanocomposites with unmodified Na⁺ montmorillonites as barrier layers for the stabilization of PSC devices.⁸⁵ Nanocomposites were prepared by solution blending and used as a thin coating (1 μm) on PET barrier foils used for the lamination of PSC cells based on poly(3-hexylthiophene):phenyl-C₆₁-butyric acid methyl ester (P3HT:PCBM). Encapsulated cells were put under continuous irradiation at 30°C and 30–40% relative humidity. The nanocomposite films produced appeared perfectly transparent in the visible range. PSC devices encapsulated with PVA nanocomposite/PET films showed a retention of PCE of about 65% after 70 h, whereas the same devices simply encapsulated with uncoated PET manifested a PCE loss of more than 80% of their initial value in the same time interval. The improvement was correlated to the better gas barrier properties of the nanocomposite/PET material.

S. Cros *et al.* tried to correlate the amount of water coming into contact with the PSC system and the corresponding loss of performance over time.⁸⁶ Both standard and inverted PSCs based on P3HT:PCBM BHJ were tested after encapsulation with different barrier foils, namely a 90 μm thick trilayer foil made of PE/(ethylene/vinyl alcohol copolymer)/PE, a 175 μm thick PET film, and a 190 μm thick quadrilayer with PP/poly(vinyl alcohol)/inorganic/PE. The decay of electrical performance of the PSC devices was correlated with the total amount of water coming into contact with the PV device, and inverted PSC devices were shown to be intrinsically more stable to water permeation than standard PSCs, likely due to the higher work function of the metallic electrodes used (Ag or Au instead of Al/Ca).

A successful case was reported by Hauch *et al.*, who used a medium-performance barrier film to encapsulate flexible P3HT:PCBM modules on PET, finding full retention of PV properties after 14 months of roof-top exposure.⁷⁹

In a more recent study, several types of inverted PSCs were encapsulated in a two-component polyurethane coating,⁸⁷ although the exact chemical composition of the coating material was undisclosed. The final product consisted of the modules embedded in the polyurethane liner between a glass front plate and a polycarbonate back sheet. The modules were exposed in eight different European countries for a period of 4.5 months. Since all modules more or less experienced the same drop in PV efficiency, even considering locations with very different sun exposure, it was concluded that photodegradation was not the major cause of degradation.

Another approach for the encapsulation of inverted PSC devices made use of a 400- μm -thick UV-curable epoxy resin to embed the PV cell using a spin-coated ZnO buffer layer to protect the photoactive materials from the epoxy.⁸⁸ The fabricated devices lost about 20% of their initial PCE after storage in the dark for two weeks.

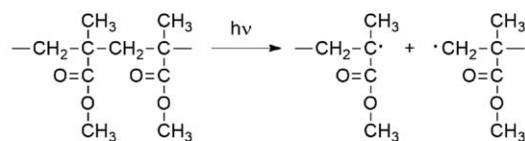
Edge sealing of PSCs is another very critical issue,⁸⁹ especially for flexible modules because water and oxygen can diffuse through the cut edges of the devices. One strategy is to provide a second level of lamination with barrier films,⁹⁰ although adhesives normally used to seal encapsulants do not show high barrier properties. To this aim, several types of polymeric adhesives based on UV-curing epoxies, polyester hot melts, and pressure-sensitive acrylics were compared for the lamination of PSCs.⁹¹ The durability of the encapsulated devices was tested over 900 h under continuous illumination. It was found that a single side encapsulation with UV curable epoxies shows the best results with a retention of about 80% of the normalized PCE.

Very recently, an innovative approach was proposed by Banerjee *et al.*, who developed a self-healing, low-permeability polyisobutylene sealant based on a reversible photoinduced crosslinking mechanism.⁹² The self-healing mechanism was verified by atomic force microscopy through exposure to direct sunlight, but no data on working PSC devices were presented.

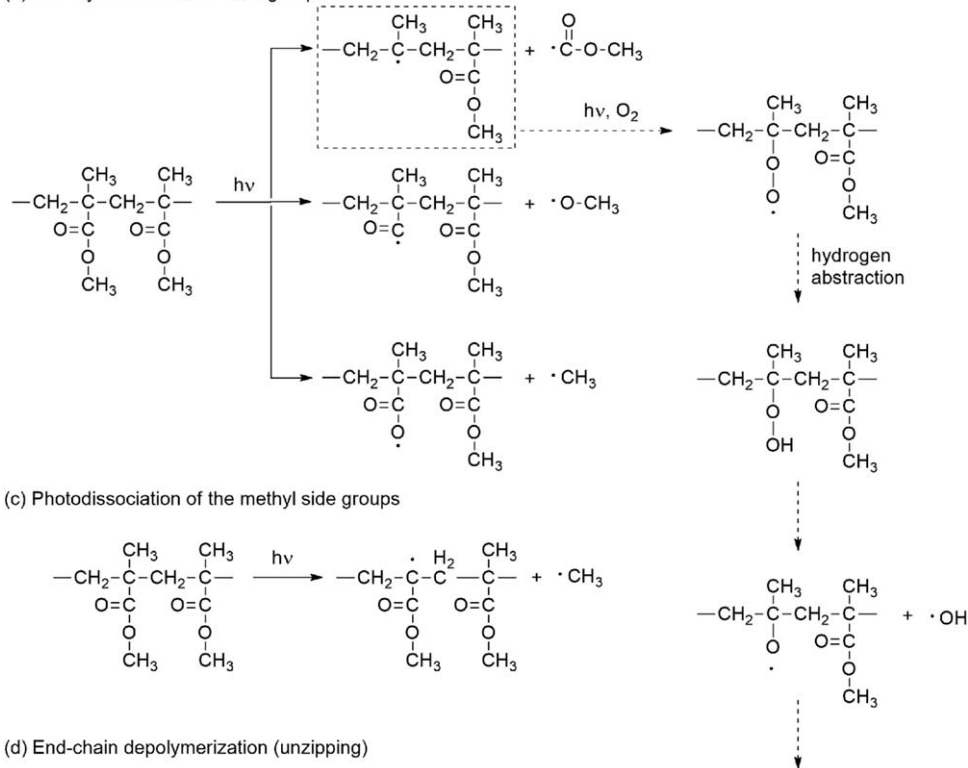
Polymeric Materials in Light-Concentration Systems

Durability of CPV Systems. In the field of solar concentration, poor outdoor durability of the materials employed for the fabrication of the optical elements that constitute the CPV system may result in a severe worsening of the optical properties of the concentrating elements and may ultimately lead to a decrease of the PV performance of the whole CPV system during the operating lifetime. Due to their size, architecture, and working principle, most CPV systems require large areas for installation so that shadowing effects can be avoided and system operation can be fully optimized. In most cases, this requirement can only be fulfilled in nonurban locations with a desert climate, where the high solar flux combined with the large space available for installation allow one to maximize CPV operation. These locations are typically characterized by severe weather conditions that include very high temperatures during daylight, large

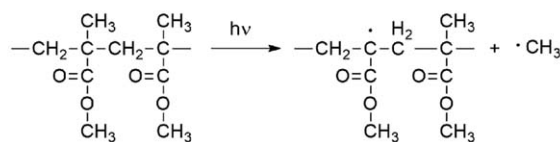
(a) Random homolytic scission of main-chain carbon-carbon bonds



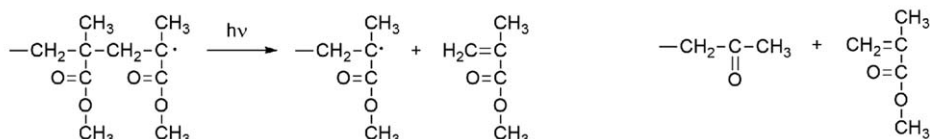
(b) Photolysis of the ester side-groups



(c) Photodissociation of the methyl side groups



(d) End-chain depolymerization (unzipping)

Scheme 2. Main photodegradation mechanisms of PMMA.^{95,97}

temperature variations between day and night, and intense winds and sandstorms, all of which pose great challenges to the durability of the CPV materials. To this end, several aspects related to the durability of the optical materials incorporated into the CPV ensemble need to be taken into consideration during its service life, including optical durability, mechanical durability, soiling, photodegradation, and thermal degradation.⁹³

Traditionally, the materials of choice for the manufacture of Fresnel lenses for use in CPV modules have been glass and acrylic polymers. While glass is obviously free from problems related to photo- and thermal stability that are instead weak points of the polymeric counterpart, the energy requirements and costs for the fabrication of glass lenses are significantly higher than those for acrylic lenses because of the higher processing temperatures needed for glass.⁹⁴ For this reason, acrylics still play a major role in the development of cost-effective CPV systems, with poly(methyl methacrylate) (PMMA) being by far

the most widely employed polymer belonging to this class of materials. The degradative behavior of PMMA has been extensively investigated in the past decades independent of CPV applications (Scheme 2), and the interested reader is invited to refer to some of the most relevant works on this topic that will not be covered in detail in this review.^{95–102}

It is, however, of interest to highlight some recent durability studies specifically focused on the use of PMMA as a building material for CPV systems. In this context, the effect of sandblasting on the transmittance of PMMA and glass as substrates for Fresnel lenses was recently evaluated as a function of the momentum of the blown sand.⁹⁴ For both substrates, the transmittance was found to decrease as a result of sandblasting. Such loss of transparency was shown to be more pronounced in the short-wavelength region, where the presence of increased surface roughness induced by sandblasting results in a higher portion of incident light being (Rayleigh) scattered.¹⁰³ The decrease in

transmittance was found to be directly correlated with the momentum of the blown sand, with PMMA being significantly more sensitive to sandblasting than the glass substrate, leading to CPV modules equipped with glass Fresnel lenses being twice as durable as PMMA lenses.

In the attempt to link the intensity and net stresses acting on materials, components, and systems to the responses observed and the degradation and damage accumulation over their lifetime, a stress and response framework can be employed, in which manifold environmental and cyclic stressors such as solar irradiance, temperature, and humidity can be simultaneously taken into account and cross-correlated to determine the degradation rates of the materials, even under accelerated conditions. Within this framework, a study of the lifetime and degradation of PV systems and materials was recently proposed on PMMA for solar mirrors and lenses.¹⁰⁴ Such an approach was based on the so-called induced absorbance to dose, a figure of merit specifically introduced for durability studies of solar and environmentally exposed materials and defined as the rate of photodarkening or photobleaching of the material as a function of radiation dose.¹⁰⁵ Accordingly, two PMMA formulations with different concentrations of UV stabilizers were exposed to two different irradiation sources characterized by a high-intensity UV component. It was found that the amount of UV stabilizer heavily influenced the level of photodarkening of the PMMA, with significantly better weatherability observed on the more heavily doped samples. A similar approach was used by the same group to investigate the degradation of back-surface acrylic mirrors used in low concentration and mirror-augmented PV systems to increase the irradiance on a module while simultaneously reducing the UV and infrared (IR) load.¹⁰⁶ In this study, PMMA mirrors were exposed to accelerated weathering (UV light), with and without humidity, and to salt-fog corrosion, and the modifications to the optical properties of the materials were analyzed within a stress and response framework.

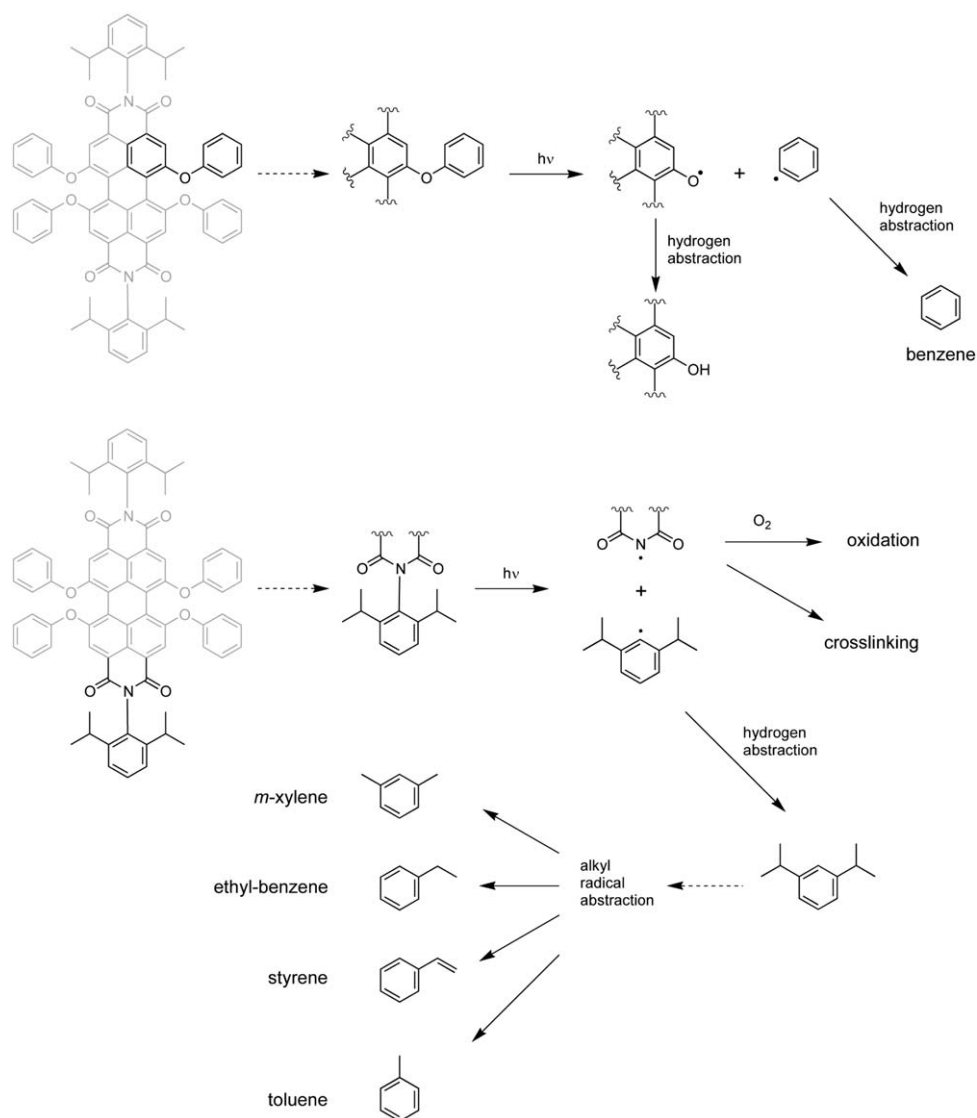
PMMA is the main polymeric material used in the CPV field, but other polymers have been investigated for potential use in CPV systems. In particular, polymeric encapsulants have found extensive use in this field as a means to couple the optical element of the CPV ensemble to the actual PV cell. As shown in the previous section, many—if not all—PV technologies require encapsulation strategies to ensure prolonged operational lifetime in an outdoor environment. In this context, the durability of several polymeric encapsulation materials, including EVA, PVB, poly(ethylene-*co*-methacrylic acid metal salt), polyethylene/polyoctene copolymer, thermoplastic polyurethane (TPU), poly(dimethylsiloxane) (PDMS), and poly(phenylmethylsiloxane), was assessed during a 12-month field exposure at the nominal optical concentration of 500 suns.¹⁰⁷ By monitoring the optical properties and the mass loss of the materials during the exposure tests, it was found that the homogeneity of the optical flux incident onto the material is critical in order to avoid local uneven discoloration in hydrocarbon polymers and in silicones, leading to reduced optical transmittance and subsequent thermal-runaway-motivated combustion. A similar degradative effect on the materials was reported in the presence of surface

contaminations such as soil, aluminum flakes, and polymer particles, thus highlighting the importance of contamination control during module and CPV ensemble manufacturing and the need for PV module sealing during field exposure.

An interesting class of polymeric materials that may potentially find extensive use in the CPV field is represented by fluoropolymers, which are characterized by excellent UV stability and outdoor durability and simultaneously display exceptional transparency.⁴⁹ The optical properties of a group of commercial fluoropolymers, including poly(tetrafluoroethylene-*co*-hexafluoropropylene), poly(tetrafluoroethylene-*co*-perfluoropropylvinyl ether), and poly(ethylene-*co*-tetrafluoroethylene), were recently investigated in terms of refractive index and haze, and their suitability for use in different applications in the PV field was discussed.¹⁰⁸

Another important area where the use of polymeric films has been explored is the heat management of CPV systems. For optimal operation, the CPV ensemble needs to be exposed to direct sunlight. However, this illumination condition causes a high flux of hot IR photons to hit the surface of the CPV components, thus leading to a significant temperature increase of the coupled PV cell, even under low-to-moderate concentration factors. Because the power conversion efficiency of PV cells is normally found to decrease with increasing temperature,⁷⁴ approaches to limit such excessive heating in CPV systems are highly desirable.⁴² To address this issue, a thermal radiation layer based on commercial acrylic polymers loaded with inorganic fillers was proposed for spray-coating deposition onto the aluminum chassis of a CPV module.¹⁰⁹ The presence of such a thermal radiation layer allowed maintainance of a 10°C lower temperature on the PV cell, in addition to improving the uniformity of the temperature distribution in the CPV module, which resulted in higher performance.

Durability of LSC Systems. In the framework of heat management for PVs, LSC systems represent a particularly interesting technology because they allow the PV cells vertically attached to the waveguide edges to operate at lower temperatures than when directly exposed to incident sunlight.¹¹⁰ This behavior is related to the fact that the typical luminescent materials employed in LSCs (i.e., organic fluorescent dyes) absorb photons in the visible range of the solar spectrum only and present Stokes shifts of a few tens of nanometers, while longer-wavelength (>700–800 nm) “hotter” photons are either transmitted through or absorbed by the polymeric waveguide, thus allowing preservation of optimal PV cell operation as compared to prolonged front-face illumination. Nevertheless, the absorbed IR photons can in principle result in a nonnegligible temperature increase in the polymeric waveguide because of the presence of IR-active functional groups that may affect the mechanical integrity (thermal expansion coefficient mismatches between waveguide and PV cell) and thermal stability of these systems. The potential effect of such thermal stresses combined with the action of typical outdoor weathering phenomena on the LSC system may lead to photo-, thermal, and mechanical degradation of the polymeric host matrix material with a consequent decline of LSC performance over time. For this reason,



Scheme 3. Proposed photodegradation mechanisms of a perylene-based commercial dye (Lumogen F Red 305, BASF) commonly employed in the field of LSCs. Adapted and reproduced from ref. 128, with permission from Elsevier.

strategies to prevent such a performance decline and to improve the durability of LSC materials and devices are of great interest in view of the potential marketability of this technology. While several studies have been focused on the maximization of LSC performance by engineering new high-efficiency/low-optical-loss device architectures^{111–119} and by synthesizing new highly performing luminescent materials,^{120–126} device stability and lifetime have been a surprisingly overlooked topic that has gained renewed interest only in the past few years.¹²⁷ In particular, only very recently the stability of organic fluorescent dyes for use in LSC systems has been investigated in detail, and potential degradation pathways have been identified (Scheme 3).^{128–130}

Together with the degradation of the luminescent dyes, another critical aspect is the miscibility of the organic luminophores in the host matrix. Indeed, organic dyes require high levels of solubility in the host medium during processing in order to avoid the formation of nonluminescent dimers and aggregates that

lead to fluorescence quenching, a decrease in luminescence quantum yield, and a drop in device performance.¹³¹ Therefore, careful selection of the appropriate luminophore/host matrix combinations is needed for optimal operations.

At present, PMMA is by far the most widely employed LSC host matrix polymer because of its favorable optical properties, processability, and cost-related characteristics.⁴⁸ However, this material is not free from drawbacks related to its relatively limited photo- and thermo-oxidative stability, especially when applied as a thin coating film, that may also induce photochemical degradation of the organic luminescent dye molecule and subsequent reduction of LSC device lifetime.¹²⁸ In recent years, different examples of new polymer-based host matrices as alternatives to PMMA have been presented in the literature, including PMMA–SiO₂ hybrids, unsaturated polyesters, polysiloxane rubbers, polylactic acid, silk fibroin, and polysilsesquioxanes.^{132–137} While some of these systems have demonstrated

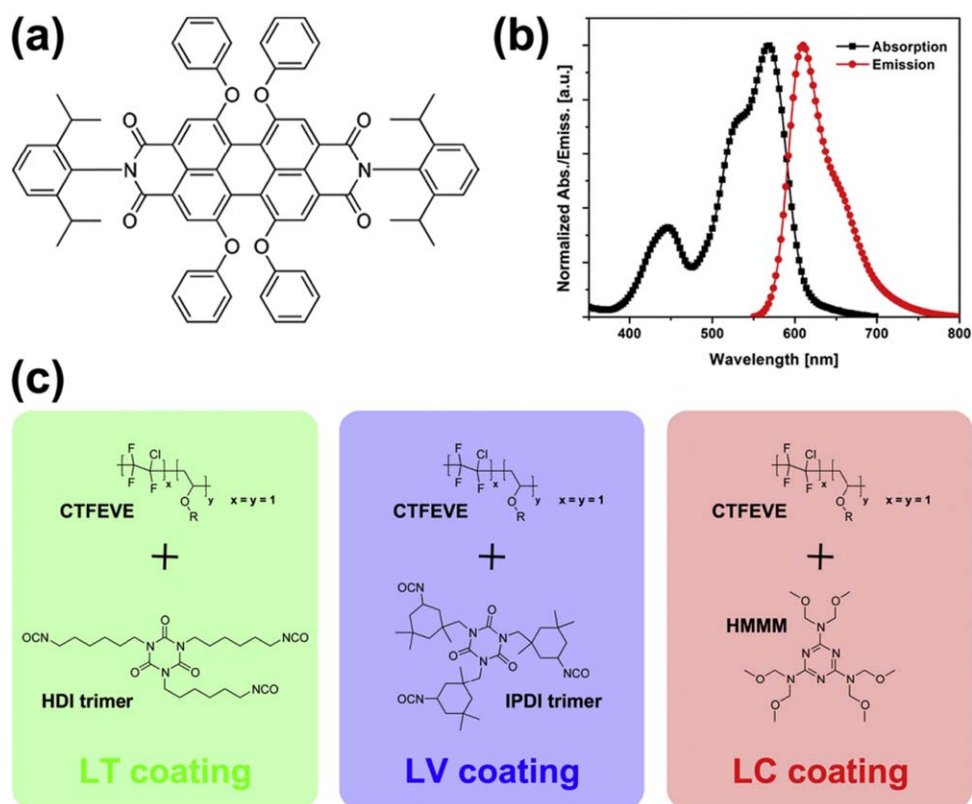


Figure 3. (a) Molecular structure, (b) absorption/emission spectra of the fluorescent organic dye employed as luminescent material, and (c) basic structural units of the materials employed to prepare the fluorinated crosslinked host matrices for thin-film LSC devices: CTFEVE – chlorotrifluoroethylene vinyl ether (some of the R groups are hydrogens, leading to the presence of reactive hydroxy groups; 100 mg KOH/g polymer), HDI, hexamethylene diisocyanate; IPDI, isophorone diisocyanate; HMMM, hexa(methoxymethyl)melamine. Reproduced from ref. 143, with permission from Elsevier. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

promising results in terms of the optical efficiency of the LSC device, no information was given on their light-exposure durability or on device lifetime.

Recently, the use of fluorinated polymers in the field of energy storage and conversion has been demonstrated.^{138,139} Fluorinated polymers are a class of high-performance materials that take advantage of the superior strength of the carbon–fluorine bond compared to the carbon–hydrogen bond to impart excellent durability, weatherability, and chemical resistance to the system.¹⁴⁰ Therefore, their use for outdoor applications represents a consolidated way to achieve high weathering resistance and long-term durability in different technological fields (e.g., architectural, marine, automotive). However, a major obstacle to the use of fluoropolymers in the LSC field is their very low solubility parameter, which determines a very limited thermodynamic miscibility in organic solvents (leading to poor processability) and with organic dyes (leading to aggregation-induced fluorescence quenching). To address these issues, the use of functional copolymers of chlorotrifluoroethylene and vinyl ethers (CTFE–VEs) thermally crosslinked with aliphatic polyisocyanates was demonstrated for the realization of high-durability host matrix materials as alternatives to PMMA in thin-film LSC systems.¹⁴¹ These CTFE–VEs show a moderately higher polarity and are soluble in some common solvents such as aromatics (xylenes) and esters, thus allowing relatively easy dissolution of

the most commonly employed luminescent organic dyes in the LSC field. In addition, the presence of —OH functionalities on these systems make them suitable to produce polyurethane coatings by combination with polyisocyanate or melamine crosslinkers.¹⁴² The incorporation of a fluorinated polymer crosslinked network as a host matrix in thin-film LSCs was shown to yield devices that maintained their initial performance during accelerated weathering (500 h), as opposed to poorly stable PMMA-based systems. These trends were correlated with the preservation of the optical properties (absorption and emission) and chemical structure (Fourier transform infrared spectroscopy) of the fluorinated host matrix upon weathering.¹⁴¹ In a further study by the same group,¹⁴³ the effect of different crosslinking agents (isocyanate versus melamine) on the chemical, physical, and morphological evolution upon accelerated weathering (1000 h) of the CTFE–VE-based luminescent coatings was examined and correlated with the functional response of the corresponding thin-film LSC devices (see Figure 3 for details on the molecular structures of the materials used). In addition, the effect of commercial light stabilizers on the weathering behavior of the LSC devices was investigated.

Very recently, a similar strategy was employed to prepare multifunctional light-managing coatings for use in the field of DSSCs.^{144,145} In particular, the presence of the —OH functional groups in the CTFE–VE copolymer resin was exploited to

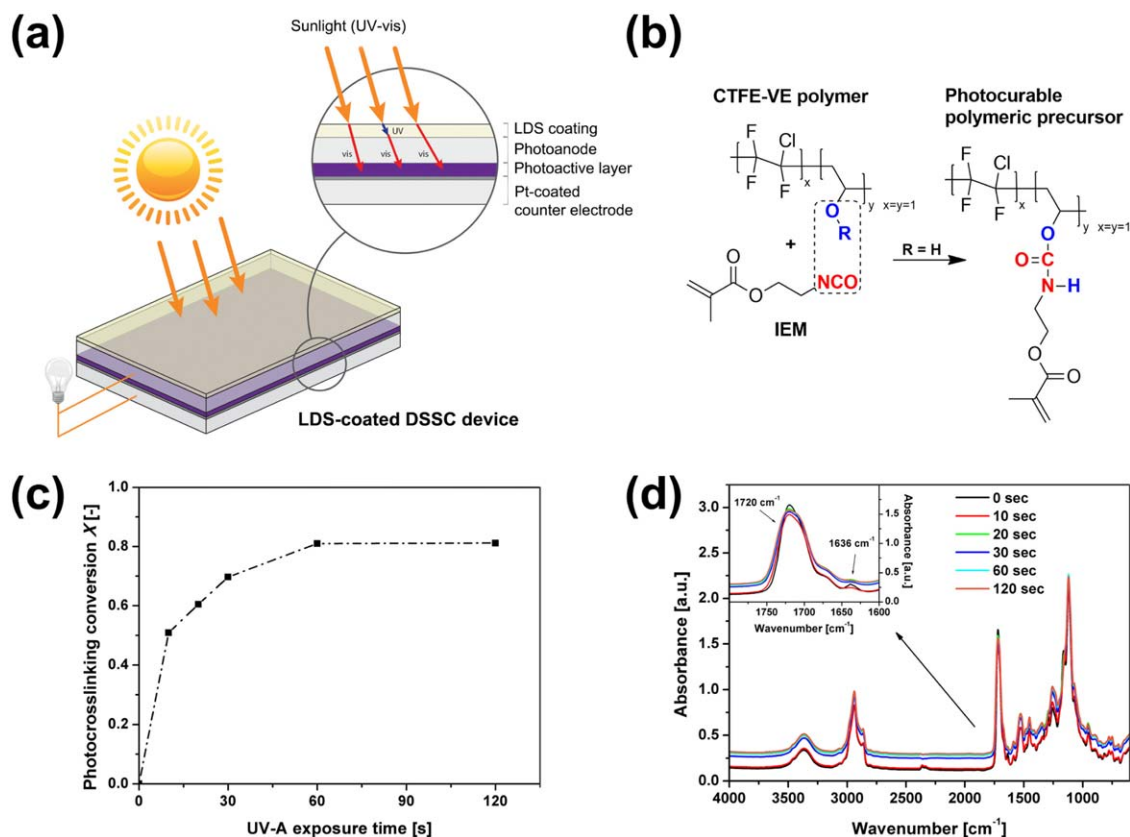


Figure 4. (a) Graphical representation of the working principle of the LDS system presented; (b) schematic representation of the mechanism of formation of the photocrosslinkable fluoropolymer precursor; (c) photocrosslinking conversion curve; and (d) FTIR spectrum of the photocrosslinked fluoropolymer at increasing UV-exposure time. The inset shows the region of the FTIR spectra where the C=C stretching signal is observed. Adapted and reproduced from ref. 145, with permission from Wiley. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

introduce UV-curable pendant methacrylic functionalities by reaction with isocyanatoethyl methacrylate (IEM) (Figure 4). As a result, multifunctional coatings incorporating different luminescent species (organic dyes or rare earth complexes) were obtained, characterized by luminescent downshifting (LDS), UV screening, and easy cleaning abilities that were shown to impart excellent durability to DSSC devices upon prolonged (>2000 h) outdoor exposure. In this context, UV-light-initiated crosslinking represents a promising approach to avoid high-temperature treatments, thus also extending the applicability of these systems to heat-sensitive flexible plastic substrates.

CONCLUSIONS AND OUTLOOK

The use of polymeric materials to improve the lifetime and durability of PV systems has increased significantly in the past few years. Key areas of application include the fields of polymer-based encapsulation materials and barrier coatings applied to different PV technologies. To this end, efforts have been addressed to conventional inorganic-based PV devices, CPV systems, and more recent technologies such as organic-based PVs and LSCs. The success of polymeric materials is to be found in the great compositional flexibility of polymers, which allows tailored optical, chemical, and mechanical proper-

ties to be achieved, thus making them theoretically suitable for any type of PV technology. In addition, their intrinsic light weight and easy processability also make them applicable on a large scale.

As shown in this review, EVA and PMMA have been considered the state-of-the-art materials in the fields of inorganic-based PVs and concentration systems and have reached commercial diffusion over a few decades. While EVA has been mainly used as an encapsulating material for PV cells and modules, PMMA has been used as a fabrication material for optical elements in CPV systems. Critical aspects related to the use of these materials in outdoor applications include their photo- (UV-induced) and thermal instability, which have been successfully addressed by employing appropriate stabilizing additives (such as UV absorbers and radical scavengers) during material formulation.

More recently, other classes of polymeric materials have entered the PV arena with the aim of overcoming some of the limitations presented by more conventional systems. In this context, partially fluorinated polymers have been shown to be very promising materials thanks to their intrinsically high photochemical and thermal stability, and some examples of these materials have appeared on the market in the last few years. More recently, some early demonstrations of the use of high-

durability multifunctional polymeric materials in the PV field have also been presented in the literature, with the aim of achieving a simultaneous improvement of both the lifetime and efficiency of PV devices.

Despite the great advancements made in the past few decades in the field of high-performing polymeric materials for improved outdoor durability of PV systems, some important aspects in this area are still to be fully investigated. In particular, the relatively limited barrier properties (OTR, WVTR) of conventional polymeric materials need to be greatly improved to meet the stringent requirements expected for new-generation organic-based devices. Furthermore, cost-effective solutions need to be implemented during the design of high-durability polymeric materials in order to minimize the cost impact on the final PV system. Novel approaches to address these issues are therefore highly desirable. In this context, the development of organic-inorganic hybrids may represent an interesting synthetic approach to boost the barrier properties of polymers by combining their typical characteristics (optical properties, mechanical flexibility, processability) with the high barrier properties of inorganic compounds. Similarly, the easy processability of polymeric materials may be exploited to develop solution-processable protective coatings to be applied *ex post* on the fabricated PV device. This approach holds particular promise in the field of flexible, organic-based PV systems, in which the use of continuous, high-throughput roll-to-roll techniques for both device fabrication and encapsulation may result in a prospective reduction of production costs.

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