Macromolecular Research, Vol. 21, No. 3, pp 248-256 (2013)
DOI 10.1007/s13233-013-1129-z

www.springer.com/13233
pISSN 1598-5032 eISSN 2092-7673

Reviews

The Solvent Problem: Redissolution of Macromolecules in Solution-Processed Organic Electronics

Carol Newby[1], **Jin-Kyun Lee**[2], **and Christopher K. Ober***[,1]

[1]*Department of Materials Science and Engineering, Cornell University, Ithaca, NY, 14853, USA*
[2]*Department of Polymer Science and Engineering, Inha University, Incheon 402-751, Korea*

Received October 30, 2012; Revised January 18, 2013; Accepted January 19, 2013

Abstract: After deposition, solution processed macromolecules are susceptible to redissolution by similar solvents. This "solvent problem" puts undesirable restrictions on the subsequent processing of organic devices; particularly when forming multiple layers or using organic patterning materials. In this review we survey the creative approaches seeking to resolve the solvent problem. We conclude that two of these approaches show promise as comprehensive solutions; use of orthogonal solvents such as hydofluoroethers, and, use of cross-linking additives. Furthering development of these or other approaches provides the community with plentiful opportunity for valuable future work.

Keywords: organic electronics, orthogonal solvent, solution processed, patterning, multilayers.

Introduction

The solubility of polymeric materials for organic electronics is both a blessing and a curse. Fabrication by solution processing is the main strategic advantage organic electronics can offer over inorganic electronics as it allows for the possibility of large-area, low-cost flexible electronics and manufacture by roll-to-roll processing. It is essentially what makes this area of research attractive. However, once a soluble organic material has been deposited it generally remains soluble. Contact with any other organic solvent will damage it at best and most likely remove it completely putting significant restrictions on subsequent processing steps. Further solution-processed organic layers cannot be deposited on top of the first, causing two problems: 1) devices with more than one stacked organic layer are prohibited, as may be desired for example in organic light emitting diodes (OLEDs), and 2) patterning that requires any type of organic resist on top of the organic layer is also prohibited as organic solvents are required for deposition, development and stripping of the resist material. This includes patterning the organic itself or patterning inorganic materials on top of it, *e.g.* by lift-off. For this reason, much of the investigative work on organic electronic materials has been done with simple single-layer device architectures. However, the body of work on more complex architectures has been growing as scientists find ways to address the solvent problem. In this review we introduce the relevant theory and survey the approaches that have been taken.

The solvent problem described is multifaceted and there is overlap with several areas that have been reviewed previously, including, polymer dissolution,[1] fabricating multilayer OLEDs,[2] patterning organics,[3,4] and synthesizing new semi-conducting polymers[5] and electroluminescent polymers.[6] Here our intention is to focus on approaches that relate specifically to the solvent, and ask how the use of damaging organic solvents is avoided, or tolerated. When it comes to processing organic small molecules, such as pentacene, the solvent problem is partially resolved as these materials can be deposited by solvent-less methods like molecular beam epitaxy. However, the problem of patterning these materials using organic resists remains. The content of this review is therefore partially relevant to small molecules but polymeric examples are used if they exist. The discussion in this article refers frequently to organic electronics, but the conclusions are generally applicable to plastic electronics or flexible electronics also.

In section I the theory of polymer solvation relevant to solution processing is introduced. Sections II, III, and IV survey the various approaches to addressing the solvent problem which fall into three categories. Section II covers methods that avoid using solvents, such as shadow masking and contact printing. Section III covers the use of alternative

---

*Corresponding Author. E-mail: cko3@cornell.edu

Table I. Comparison of Techniques that Address the Solvent Problem[a]

Technique	Bilayers?	Pattern Organic?	Pattern on Organic?	Resolution	Device(s) Fabricated	Ref(s)
II. Avoiding Solvents						
High Resolution Shadow Masking			✓	75 nm	Biosensor	11,12
Resist Bridge			✓	100 nm	OTFT	13,14
Strippable Mask		*	✓	40 μm		15
Additive Metal Contact Printing			✓	500 nm	OTFT	16
Additive Org Contact Printing		✓		?†	OTFT	17
Add./Sub. Org Contact Printing		✓		10 μm	OLED	18
Multi Add. Org Contact Printing	✓	✓		?†	OTFT	19
Paralyene Barrier Layer		✓	✓	1 μm	OTFT	20
Cytop Barrier Layer		✓	*	2 μm	Junction	21,22
Al_2O_3 Barrier Layer		✓	✓	?†	OLED	23
PVA/PMMA Barrier Layers		*	✓	?†	OTFT	24
Self-Patternable Conductor		✓	✓	?†	OTFT	25
Self-Patternable LE Polymers		✓		?†	OLED	26,27
Self-Patternable LE Polymers		✓		?†		29
III. Alternative Solvents						
Water-Soluble Organics	✓			-		30
Supercritical CO_2		✓		1.3 μm	OLED	31
Hydrofluoroethers		✓	✓	80 nm	OTFT	33-36
Fluorinated LE Polymers	*	✓	✓	100 μm	OLED	38-40
Interlayer Lithography		✓		2 μm	OTFT	41,42
Non-Chlorinated Solvents				-	OTFT	43
IV. Resistance to Solvents						
Thermal Crosslinking	*	*	*	-	OLED	44
Cross-Linkable Side Chains	*	✓	*	55 μm	OLED	45,46
Cross-Linking Additive	✓	*	*	-	OPV	47

[a] *: possible but not demonstrated. †: not reported. LE=light emitting. OLED=organic light emitting diode. OTFT=organic thin film transistor. OPV= organic photovoltaic cell.

solvents which are chemically orthogonal to organic materials and therefore non-damaging. Section IV covers approaches that create resistance to organic solvents, principally by some form of cross-linking. We end with a conclusion section that weighs up the merits and drawbacks of the methods reviewed, speculates on possible future developments and includes Table I which summarizes the capabilities of all approaches included in this review.

Section I: Polymer Dissolution

The solvent is typically only a vehicle for deposition and no solvent molecules remain in the finished device. However, the properties of the solvent have important implications in all stages of solution processing including: 1) solvation of the material to be deposited, 2) processability of the solution, and 3) solidification of the material *via* evaporation. There have been innovations in solvent use driven by the second and third stages. For example, different microstructures have been achieved simply by changing the solvent - Duong *et al.* looked at this recently in relation to bulk heterojunctions.[7] There has also been significant work on using solvent-vapor annealing to control microstructure[8] and improve device performance.[9] But our focus is solvent compatibility and we are largely concerned with the first stage of solution processing - solvation. We seek to understand why one solvent will dissolve one polymer but leave another unaffected.

The solvation of a solute (polymer) by a solvent is governed by the energy of free mixing,[10]

$$\Delta G_m = \Delta H_m - T\Delta S_m$$

where ΔG_m is the Gibbs free energy of mixing, ΔH_m is the enthalpy of mixing, T is the temperature (K) and ΔS_m is the entropy of mixing. If ΔG_m is negative the polymer will dissolve in the solvent, if it is positive it will not. The dilute solutions of conjugated polymers used in organic electronics do not behave as ideal solutions. Therefore, reaching precise values for the entropy of mixing is not straightforward, yet it is fair to assume that it is small and that solubility is largely determined by the enthalpic contribution. Although, the entropy of mixing still decreases with increasing chain length making low molecular weight polymers generally easier to dissolve.

A simple expression for the enthalpy of mixing is given by,

$$\Delta H_m = V(\delta_1 - \delta_2)^2 \Phi_1 \Phi_2$$

where V is the volume of the mixture, Φ_i is the volume fraction of molecule i, and δ_i is the Hildebrand solubility parameter of i, defined as,

$$\delta = \sqrt{\frac{E}{V}}$$

where E is the cohesive energy, and is effectively a sum of all the intermolecular forces. It can be seen that the smaller the difference between the solubility parameters of the polymer and solvent, the smaller the enthalpy of mixing, therefore leading to a greater tendency to solvate. This is the origin of the phrase “like dissolves like”. The cohesive energy is often broken down further into contributions from dispersive (D), polar (P) and hydrogen bonding (H) forces as these are the three most dominant forces in polymers,

$$E = E_D + E_P + E_H$$

The contributions of these forces are directly determined by the chemical nature of the polymer and the solvent. Because polymer solubility is affected by many interactions, it is difficult to calculate or predict. Therefore, determining whether a liquid is a good solvent for a polymer is usually done experimentally *via* a trial-and-error approach. This can be time consuming and not always conclusive-polymers can take hours or days to fully dissolve, and even then it may be hard to distinguish between a fine suspension and a completely homogeneous solution. But some are starting to use more quantitative approaches, such as Duong *et al.* who calculate solubility parameters for a range of common organic systems.[7] Studies such as the one by Duong *et al.* will become increasingly valuable as the community seeks to optimize device performance and look towards manufacturing.

Section II: Avoiding Solvents

Our search for a solution to the solvent problem starts by examining the simplest solution possible - avoiding use of solvents completely. There are some restricted fabrication techniques in which the deposited organic material does not come into contact with organic solvents in further processing steps. These include shadow masking, contact printing and the use of barrier layers. So called “self-patternable” materials are also included in this section as they reduce the number of processing steps and therefore lessen the possibility of redissolution.

Shadow masking uses simple physical masks cut into a metal sheet and avoids using solvents completely. This technique has been the workhorse patterning technique to thermally deposit metal electrodes on top of organics with dimensions of tens of microns. Although it can be used to pattern on top of organic materials *via* thermal evaporation, it does not solve the problem of fabricating multiple organic layers. Low resolution is the main drawback of shadow masking, but this can be improved by the fabrication of more sophisticated masks.

The highest resolution achieved with shadow masking used masks etched into suspended silicon nitride membranes. Metal dots and lines as small as 16 nm across are demonstrated on inorganic substrates.[11] Vazquez-Mena *et al.* recently used similar silicon nitride masks to fabricate 25 nm dots and 75 nm lines on polymer substrates including polyimide, paralyene, polydimethylsiloxane (PDMS) and SU-8 photoresist.[12]

Tukagoshi *et al*. use a related approach to form an undercut resist bridge that is in contact with the substrate.[13] They did this using a spin-coated trilayer resist system of poly(methyl methacrylate) (PMMA) (950k)/PMMA (495k)/MMA exposed with electron beam lithography. The lower layers have greater solubility in the developer resulting in an undercut profile which clears completely and forms a bridge if the feature is small enough. An organic semiconductor then metal contacts are deposited by evaporation and the resist bridge structure is left in place. In collaboration with Ante *et al.* this technique is used to fabricate organic transistors with sub-100 nm channel lengths.[14]

Another variation on the theme of shadow masking is the demonstration of a “strippable mask”[15] by Ogihara *et al.* They electrodeposited nickel films onto a conductive indium tin oxide substrate pre-patterned with photoresist. After stripping the resist, organic materials are drop-cast on the nickel mask which has sufficient mechanical strength to then be stripped in one piece. Patterning of carbon nanotubes and titania nanoparticles is demonstrated. Examples did not include any organics but this technique could presumably be extended to patterning organics.

Contact printing uses a prefabricated stamp, often made of polydimethylsiloxane (PDMS), with raised features that can vary in size from several hundred microns down to a few microns or even hundreds of nanometers. The stamp can either be loaded with a material and applied to the substrate for additive patterning, or used as-formed for subtractive patterning. Of great importance is the control of adhesion forces between the material to be deposited and the stamp, and how they compare to those forces between the material to be deposited and the substrate. These can be tuned to some extent by the use of surface treatments and modification by self-assembled monolayers, often making the stamp specific to a certain material. Limited scope to vary the specificity of these adhesion forces ultimately restricts the range of materials that can be deposited in this way. Also, the effect of subjecting underlying layers to applied pressures is unknown but unlikely to be beneficial.

Loo *et al.* use PDMS, fused silica and gallium arsenide (GsAs) stamps for additive contact printing of gold features on PDMS-coated polyethylene terephthalate (PET) substrates.[16] Gold then a thin layer of titanium are evaporated on the stamp. The gold adheres poorly to the stamp and the titanium improves adhesion to the substrate. 500 nm wide lines are achieved with the GaAs stamp. This technique is used to fabricate top-contact pentacene transistors that are shown to operate comparably to ones fabricated by shadow masking.

Additive contact printing of an organic is shown by Park *et al.*, also using a PDMS stamp.[17] The stamp is “inked” by drop-casting poly(3-hexylthiophene) (P3HT) from chloroform and dried with a flow of nitrogen. The P3HT is then stamped onto a prefabricated bottom-contact transistor architecture, the surface being predominantly silicon dioxide. The thickness of the printed P3HT can be varied from 100-500 nm but the lateral resolution is not reported.

Granlund *et al.* demonstrated subtractive (and additive) patterning of polymers using a PDMS stamp.[18] Poly(3,4-ethylenedioxythiophene) (PEDOT) is spin coated from a water and glycerol mixture on to glass, then pressed against a PDMS stamp which removes sections leaving lines patterned down to 10 μm.

As well as simply patterning organic layers contact printing can also be used to form organic bilayer structures. Li and Guo demonstrate forming PEDOT electrodes on pentacene by contact printing.[19] Again, a PDMS stamp is used and top contact pentacene transistors are made with 2 μm channel lengths.

Protective barrier layers can be used to prevent redissolution of a deposited material. Barrier layer materials must be impervious to the solvents used and non-damaging to the underlying organic. As these requirements are not particularly strict a wide range of materials have potential to be barriers on an equally wide range of organic active materials. A key issue is the removal of the barrier layer after processing which can be difficult when use of organic solvents is not an option. Complications include damage to and contamination of the underlying organic.

DeFranco *et al.* use parylene as a barrier layer.[20] Deposited by chemical vapor deposition it forms an inert, pin-hole free film impervious to organic solvents. Patterning with conventional organic resists and solvents can then take place on top of the parylene and patterns are transferred to the organic, through the parylene, by a dry etching step. The parylene layer can then be mechanically peeled off leaving the patterned organic. Pentacene, PEDOT and ruthenium tris-bipyridine features down to 1 μm are demonstrated.

Dhar *et al.* use a similar technique but with Cytop as their barrier layer.[21] Cytop has the advantage of being solution processible from fluorosolvents which are chemically orthogonal to organic materials - these are discussed further in Section III. Dhar *et el.* demonstrate its use with P3HT and an *n*-type organic small molecule, naphthalene tetracarboxydiimide, in order to study lateral organic heterojunctions. Chang *et al.* also used a Cytop barrier layer to fabricate lateral organic heterojunctions.[22]

Another work uses a 1.2 Å inorganic barrier layer of Al_2O_3 deposited by atomic layer deposition (ALD).[23] This is deposited on top of poly[1-methoxy-4-(20-ethyl-hexyloxy)-2,5-phenylene vinylene] (MEH-PPV) which is solution processed from toluene. In this case the barrier layer both protects the underlying organic during lithographic processing and improves device function as the Al_2O_3 acts as an electron injection/hole blocking buffer layer in the OLED devices fabricated.

Kuo and Jackson demonstrate a system that uses three polymeric barrier layers[24] all formed by spincoating. Water soluble poly(vinyl alcohol) (PVA) is deposited on top of the organic to protect it from organic solvents. A poly(methylmethacrylate) (PMMA) layer protects the PVA during a later developing step that uses an aqueous base. A cross-linked PVA layer is used to prevent intermixing between the PMMA and a conventional organic resist. Patterning can then be conducted on top of the PVA/PMMA/PVA stack using conventional photolithography. The pattern is transferred through the top two barrier layers and half of the lower PVA layer by a dry etch, then the organic is revealed with a final water etch. Metal contacts can be deposited and the resist stack removed by lift-off in water. This technique is used to fabricate top-contact pentacene transistors with channel lengths down to 6 μm. Aside from complexities arising from using so many layers, there is no way to precisely time the water etch step such that the organic is exposed but the resist stack does not begin to lift off. Exposure of the organic to water may also be detrimental.

Self-patternable materials are active materials that incorporate some photoresist-like properties such that they are functional but also responsive to light in a way that makes them patternable. Use of self-patternable materials reduces the number of processing steps and therefore offers a route to avoiding redissolution of organics - they can be patterned without spincoating and developing photoresist on top. One way to achieve self-patterning is to induce crosslinking reactions which, in this review, are covered in Section IV on resistance to solvents. In this section the self-patternable materials discussed respond to light either with a change in solubility or a change in functional properties.

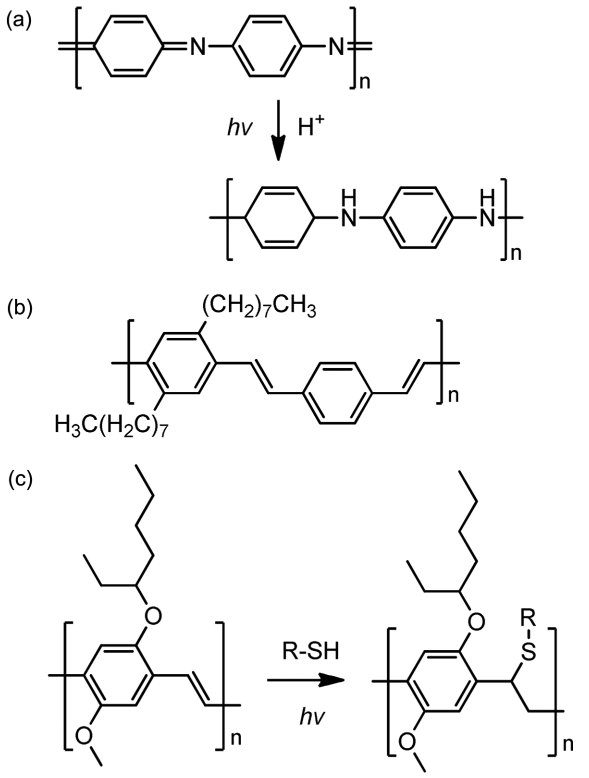

Figure 1. Chemical structures and photoreactions of the self-patternable materials reviewed, including, (a) protonation of PANI, (b) structure of photobleachable dioctyl-substituted PPV, and, (c) thiol-ene type photobleaching of MEH-PPV. Adapted from Refs. 26 and 28.

The self-patterning approach is demonstrated by Drury *et al.* using doped polyaniline (PANI) films.[25] A photo acid generator is included in spincoated films of PANI that, when exposed to light, protonates the PANI rendering it significantly less conductive, as shown in Figure 1(a). Unexposed regions with a sheet resistance of 10^3 Ω/sq changed to 10^{14} Ω/sq after exposure to ultra violet (UV) radiation. The PANI layer is used to form the electrodes of bottom-contact all polymer transistors with 2 μm channel lengths.

Self-patterning of light-emitting active layers can be achieved by photo-bleaching. Krebs and Jørgensen adapted polyphenylenevinylene (PPV) to make it photobleachable in air on exposure to UV.[26] Dioctyl- and didodecyl-substituted PPV, as in Figure 1(b), are shown to degrade during exposure. The authors hypothesize that this occurs by the cycloaddition of oxygen to the vinylene groups. Krebs and Spanggaard later demonstrated the use of this technique to fabricate and test OLED structures.[27] After photo-bleaching, metal contacts are deposited on top to form complete devices (and the photobleached material remains in place). A later work by Vasilopoulou *et al.* uses a similar approach, but interestingly, the emission color can be tuned from red through to green and then blue by varying the exposure dose.[28]

Pogantsch *et al.* show that MEH-PPV mixed with dodecanethiol is self-patternable.[29] When exposed, a photo-induced thiol-ene reaction occurs saturating the vinylene units and causing photo-bleaching, see Figure 1(c). The authors ingeniously extend this concept to a blend of MEH-PPV and poly(9,9′-dioctylfluorene) (PF8) such that the emission color can be tuned from green to blue *via* patterning.

Unfortunately, the techniques in this section on avoiding solvents are for the most part tailored to specific applications or materials. Shadow masking is restricted to patterning on organics; contact printing is material specific due to adhesion forces; barrier layers are material specific due to interlayer interactions; self-patterning properties are restricted to just a few chemical structures. There are also other concerns that would hinder their widespread use: shadow masking is difficult to align to other layers, barrier layers are difficult to remove and very few molecules are self-patternable. To develop more sophisticated and general techniques solvents are necessary and close attention must be paid to their selection.

Section III: Alternative Solvents

Chemical orthogonality can be used to address the solvent problem. When a certain material dissolves well in some solvents and is unaffected by others, processing steps can be carried out using these so-call ‘orthogonal’ solvents. For organic electronics, orthogonal solvents must generally be non-organic. Solubility in organics originates from their lack of polarity, so an orthogonal solvent can be one with significant polarity, such as water. Water soluble active materials can be used to form organic bilayers,[30] but they do not resolve all issues; conventional resists often use an aqueous developer which can damage water-soluble layers. Another solvent option is super critical carbon dioxide ($scCO_2$) which is not polar and a poor solvent for most organic materials. $ScCO_2$ is being used increasingly in a variety of industries as a non-toxic alternative to organic solvents, but a major drawback is the need for specialized equipment to get CO_2 to the necessary temperatures and pressures for super critical behavior. Further options for orthogonal solvents arise when other intermolecular forces, other than polarity, are considered. Fluorinated solvents have unusually low London dispersion forces due to fluorine’s high electronegativity. This is enough to make them immiscible with organic and aqueous solutions and therefore non-damaging to organic materials.

Water-soluble conductive polymer PEDOT is routinely used in organic devices as an injection layer, but use of other water soluble polymers is less common. Gong *et al.* use PEDOT and other polymers to fabricate white polymer light emitting diodes consisting of three layers that are aqueous/organic/aqueous.[30] The device consists of a water-soluble hole transport layer spincoated on top of PEDOT, followed

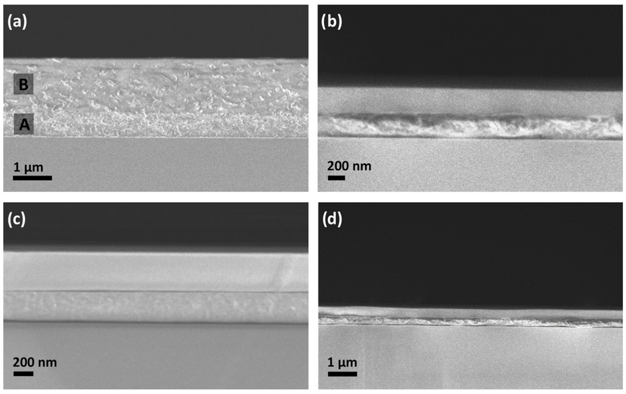

Figure 2. SEM images of cleaved cross sections of spincoated bilayers on silicon substrates. (a) shows intermixing when an organic is deposited on top of another organic using the same solvent (first layer: 20 mg/mL P3HT in chloroform, second layer: 50 mg/mL PMMA in chloroform), the interface is uneven and the layers are mixed but a clear distinction in contrast can be seen between a lower P3HT-rich region and an upper PMMA-rich region that has picked up flakes of P3HT. (b) shows no intermixing when a fluoropolymer is deposited from hydrofluoroethers on top of an organic layer (first layer: 20 mg/mL P3HT in chloroform, second layer: 50 mg/mL poly(decafluoromethacrylate) (PFDMA) in HFE 7500), (c) another example of orthogonal bilayers (first layer: 50 mg/mL PFDMA in HFE 7500, second layer: 50 mg/mL PMMA in chloroform), (d) same as (b) but at lower magnification.

by an organic-soluble emissive blend of two polymers and a metal complex, and finally, a water-soluble electron transporting layer. This is a nice demonstration of the use of orthogonality to achieve multilayer organic devices, but it does not offer the possibility of patterning these devices.

Supercritical carbon dioxide is a poor solvent for most organic materials but has a high affinity for fluorocarbons. Hwang *et al.* developed a copolymer photoresist[31] composed of *tert*-butyl methacrylate (TBMA), to provide patternability, and 1*H*,1*H*,2*H*,2*H*-perfluorodecyl methacrylate, to provide solubility in $scCO_2$. Negative tone images are formed through deprotection of the TBMA and development in $scCO_2$. After pattern transfer into the underlying organic *via* reactive ion etching, treatment with hexamethyldisilazane is used to re-protect the TBMA so the remaining resist could also be stripped in $scCO_2$. The authors demonstrated patterns down to 1.3 μm and fabrication of OLEDs.

Fluoropolymers are also soluble in fluorinated solvents which do not require the high pressures and temperatures that $scCO_2$ does. Well-known families of fluorinated solvents include low molecular weight hydrofluorocarbons and hydrofluoroethers (HFEs); although the former are undesirable for environmental reasons. HFEs, on the other hand, have zero ozone depleting potential and low values of global warming potential.[32] HFEs can therefore be used in ‘orthogonal processing’ to form bilayers of organic materials that do not suffer from intermixing, as shown in Figure 2. Our group at Cornell first demonstrated the use of HFEs to process a fluorinated small-molecule resist on top of organics.[33] We then go on to expand this work with HFEs is several directions. A polymeric fluorinated photoresist is developed[34] which is also non-chemically amplified so that acidic materials like PEDOT do not interfere with resist function.[35] The fluorinated small molecule resist, a resorcinarene, is used in multilevel patterning of more than one organic layer, and, in combination with e-beam patterning, can demonstrate negative-tone 80 nm features.[36] Alternatively, active materials with a high degree of fluorination are developed such that they can be deposited from HFEs and are not damaged by conventional photoresists.[37,38] The materials developed comprised a set of light-emitting fluorinated polyfluorenes copolymerized with various moieties to achieve emission in the red, green and blue. With this diverse set of orthogonal solvents, materials and resists our group is able to fabricate a wide range of devices including top-contact P3HT transistors with 200 nm channel lengths and 12-stage ring oscillators based on pentacene transistors.[39,40]

Huang *et al.* developed a process they termed ‘interlayer lithography’ that patterns an organic resist under a water-soluble active material like PEDOT *via* lift-off.[41] Further active organic layers can be deposited on top of the PEDOT layer and patterned in the same lift-off step provided they are compatible with the developing solvent. SU-8 photoresist is used in this way to pattern PEDOT and multiple polyfluorenes to 2 μm features on silicon, glass and flexible plastic substrates with lift-off in propylene glycol methyl ether acetate (PGMEA). Leem *et al.* used interlayer lithography to fabricate PEDOT transistors also.[42] Drawbacks include having to expose the active material to UV in the process of exposing the underlying resist, the active material having to be resistant yet permeable to the developer and the resist remaining in place after patterning.

Just as environmental considerations influence which fluorosolvents to use environmental considerations may also be a factor to consider when it comes to other solvents commonly used in processing organic electronics. Liu *et al.* sought to avoid the use of chlorinated solvents in the fabrication of P3HT organic thin film transistors (OTFTs) and developed polythiophene derivatives processible in benign alternatives such as tetrahydrofuran, toluene and xylene.[43] Using this system they fabricate transistors with mobilities up to 0.18 $cm^2 V^{-1} s^{-1}$.

Of the alternative solvents considered, HFEs are most appealing. Their orthogonality to organics provides an ‘extra dimension’ in which patterning steps can be conducted. Fluorinating the active layer does offer a route to making multiple layers without intermixing, but synthesizing suitable new polymers is laborious. Also, inclusion of fluorine, a highly electronegative atom, in an active material risks reducing mobility or even creating traps. Using orthogonal solvents

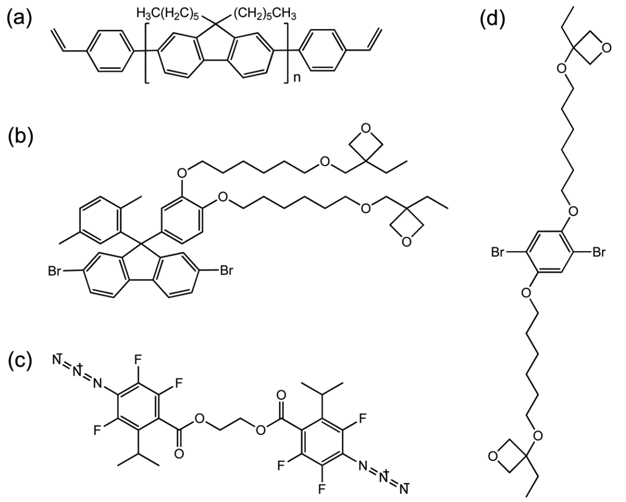

Figure 3. Chemical structures of the cross-linkable materials reviewed, including (a) polyfluorene with thermally cross-linkable end groups, (b) oxetane-functioalized moiety used in the synthesis of cross-linkable polyfluorenes by Müller *et al.* (c) cross-linking additive ethylene bis(4-azido-2,3,5-trifluoro-6-isopropylbenzoate) and (d) oxetane-functioalized moiety used by Charas *et al.* Adapted from Refs. 43-46.

means the organic is resistant to a certain set of solvents, but the deposited material can be made resistant to more than just one type of solvent through crosslinking.

Section IV: Resistance to Solvents

Crosslinking polymeric active layers after deposition can be used to make then insoluble and it is certainly advantageous that they are then resistant to all solvents (except, possibly, for some swelling). The challenge is to restrict crosslinking to parts of the molecule that are not conjugated because crosslinking that interferes with or interrupts the conjugated π-system can negatively affect electrical and optical properties.

It is worth mentioning the role of baking at this point. Baking or annealing a material deposited from solution may well reduce the rate and/or extend of redissolution during deposition of a second layer, but will not eliminate it completely. It is likely that device performance is negatively impacted by the disordered interfaces that result from intermixing, but we know of no extensive study of its effects in organic electronics.

Klärner *et al.* developed a method to end-cap polyfluorene chains with thermally crosslinkable groups,[44] as shown in Figure 3(a).The vinyl end groups can be crosslinked by annealing at 175-200 °C in an air-free environment to yield an insoluble layer with unchanged emission properties (presumably because the cross-linking density is so low).

Polyfluorenes are also worked on by Müller *et al.* who develop a set of polymers with crosslinkable side chains.[45] The fluorene monomer is copolymerized with moieties to both achieve red, green and blue emission and another oxetane-functionalized moiety (Figure 3(b)) to make the materials photosensitive. On exposure to UV light an ionic photoacid generator produced H^+ opening the oxetane ring and initiating cross-linking. As this approach also allows patterning, an OLED with red, green and blue pixels is fabricated *via* multiple patterning steps. More recently Charas *et al.* also developed similar polyfluorenes with oxetane sidechains[46] but used an oxetane functionalized phenylene monomer to give the sidechains more mobility, see Figure 3(d).

Approaches discussed so far have all dealt with a specific functional polymer, but the utility of the crosslinking approach would be significantly increased if it could be applied more generally. Png *et al.* have developed such a technique that uses a bis(fluorophenyl azide), shown in Figure 3(c), as a separate additive to photocrosslink the alkyl sidechains of any conjugated polymer.[47] Interestingly, this approach is then used in the fabrication of bulk heterojunctions (BHJs) for photovoltaic cells, rather than OLEDs or OTFTs as in most other cases. An initial BHJ is deposited with only one phase containing the crosslinker so that the second phase could be washed out and replaced with another material.

Cross-linking that can be applied to any material resulting in resistance to all solvents is an exciting prospect. The key question is whether cross-linking can realistically be extended to other systems without compromising their functional properties, or is it inevitable that the conjugated system will always be interrupted to some small extent? The use of crosslinking for OPV fabrication also suggests that the applications of a solution to the solvent problem could go beyond the patterning and multilayer formation discussed in this review.

Conclusions

The solvent problem, namely that deposited organics remain soluble in organic solvents, has important implications for the fabrication of organic devices. The solvent being just a vehicle for deposition or removal, means the choice of solvent is often overlooked. The authors suspect that gains can be made in the field if the solvent choice and effects are given more careful consideration. As well as affecting microstructure and properties, it is really the solvents used that determine the processibility of organic materials - whether they can be patterned or used in multilayer architectures.

This review finds that current solutions to the solvent problem are varied and often creative. The majority of approaches have been developed for a specific material or device and their application to a broader range of materials is not investigated, although this would be of great interest. The approaches are split; some allow for the fabrication of multiple ‘stacked’ organic layers, others allow for patterning of, or on, organic materials. Considering that the ultimate goal of this area of research is the large scale manufacture of organic/flexible electronics, the successful approach is likely to be one that allows for both multilayer formation and patterning, and is widely applicable to the majority of commonly used organic materials. This may seem like a tall order, and if it is not possible an adoption of a combination of approaches is likely, but development of a comprehensive solution cannot yet be ruled out.

To facilitate comparisons Table I shows a summary of the techniques reviewed and whether they allow bilayer formation, patterning of organics, or pattering on organics. The types of device that served as the end goal for most publications varied, so some techniques are, in our opinion, capable of more than is reported. The resolution achieved in patterning is included in the table if it is reported, but this value is often not optimized, especially in the case of OLED applications, and it is debatable whether organic/flexible electronics is really in need of high-resolution patterning.

Of the approaches in this review, two have the potential to become comprehensive solutions. These are, the use of orthogonal hydrofluoroether solvents, and, the use of a cross-linker additive like bis(fluorophenyl azide). Both show, in a combination of publications, promising abilities and wide application. However, the hesitation with both approaches is that they are likely to negatively affect the active materials' properties. If these issues are successfully addressed it could lead to the desired comprehensive and general solution to the solvent problem.

Acknowledgments. This manuscript was accomplished with the support of the National Science Foundation (Materials World Network DMR-0908994). JKL thanks Inha University for financial support. This work was performed in part at the Cornell NanoScale Facility, a member of the National Nanotechnology Infrastructure Network, which is supported by the National Science Foundation (Grant ECS-0335765).

References

(1) B. A. Miller-Chou and J. L. Koenig, *Prog. Polym. Sci.*, **28**, 1223 (2003).
(2) K. T. Kamtekar, A. P. Monkman, and M. R. Bryce, *Adv. Mater.,* **22**, 572 (2010).
(3) E. Menard, M. A. Meitl, Y. Sun, J.-U. Park, D. J.-L. Shir, Y.-S. Nam, S. Jeon, and J. A. Rogers, *Chem. Rev.*, **107**, 1117 (2007).
(4) Y. Xu, F. Zhang, and X. Feng, *Small,* **7**, 1338 (2011).
(5) A. Facchetti, *Chem. Mater.*, **23**, 733 (2011).
(6) A. C. Grimsdale, K. L. Chan, R. E. Martin, P. G. Jokisz, and A. B. Holmes, *Chem. Rev.*, **109**, 897 (2009).
(7) D. T. Duong, B. Walker, J. Lin, C. Kim, J. Love, B. Purushothaman, J. E. Anthony, and T.-Q. Nguyen, *J. Polym. Sci. Part B: Polym. Phys.*, **50**, 1405 (2012).
(8) D. J. Gundlach, T. N. Jackson, D. G. Schlom, and S. F. Nelson, *Appl. Phys. Lett.*, **74**, 3302 (1999).
(9) K. C. Dickey, J. E. Anthony, and Y.-L. Loo, *Adv. Mater.,* **18**, 1721 (2006).
(10) R. J. Young and P. A. Lovell, in *Introduction to Polymers*, 3rd ed., CRC Press, Boca Raton, 2011, p 688.
(11) M. M. Deshmukh, D. C. Ralph, M. Thomas, and J. Silcox, *Appl. Phys. Lett.*, **75**, 1631 (1999).
(12) O. Vazquez-Mena, T. Sannomiya, M. Tosun, L. G. Villanueva, V. Savu, J. Voros, and J. Brugger, *ACS Nano*, **6**, 5474 (2012).
(13) I. Yagi, K. Shigeto, K. Tsukagoshi, and Y. Aoyagi, *Jpn. J. Appl. Phys.*, **44**, L479 (2005).
(14) F. Ante, D. Källblein, U. Zschieschang, T. W. Canzler, A. Werner, K. Takimiya, M. Ikeda, T. Sekitani, T. Someya, and H. Klauk, *Small,* **7**, 1186 (2011).
(15) H. Ogihara, M. Fukasawa, and T. Saji, *ACS Appl. Mater. Interfaces*, **3**, 2108 (2011).
(16) Y.-L. Loo, R. L. Willett, K. W. Baldwin, and J. A. Rogers, *Appl. Phys. Lett.*, **81**, 562 (2002).
(17) S. K. Park, Y. H. Kim, J. I. Han, D. G. Moon, and W. K. Kim, *IEEE Trans. Electron Devices*, **49**, 2008 (2002).
(18) T. Granlund, T. Nyberg, L. Stolz Roman, M. Svensson, and O. Inganäs, *Adv. Mater.*, **12**, 269 (2000).
(19) D. Li and L. J. Guo, *Appl. Phys. Lett.*, **88**, 063513 (2006).
(20) J. A. DeFranco, B. S. Schmidt, M. Lipson, and G. G. Malliaras, *Org. Electron.*, **7**, 22 (2006).
(21) B. M. Dhar, G. S. Kini, G. Xia, B. J. Jung, N. Markovic, and H. E. Katz, *Proc. Natl. Acad. Sci. U.S.A.*, **107**, 3972 (2010).
(22) J.-F. Chang, M. C. Gwinner, M. Caironi, T. Sakanoue, and H. Sirringhaus, *Adv. Funct. Mater.*, **20**, 2825 (2010).
(23) C.-Y. Chang, F.-Y. Tsai, S.-J. Jhuo, and M.-J. Chen, *Org. Electron.*, **9**, 667 (2008).
(24) C.-C. Kuo and T. N. Jackson, *Appl. Phys. Lett.*, **94**, 053304 (2009).
(25) C. J. Drury, C. M. J. Mutsaers, C. M. Hart, M. Matters, and D. M. de Leeuw, *Appl. Phys. Lett.*, **73**, 108 (1998).
(26) F. C. Krebs and M. Jørgensen, *Macromolecules*, **36**, 4374 (2003).
(27) F. C. Krebs and H. Spanggaard, *Synth. Met.*, **148**, 53 (2005).
(28) M. Vasilopoulou, D. Georgiadou, G. Pistolis and P. Argitis, *Adv. Funct. Mater.*, **17**, 3477 (2007).
(29) A. Pogantsch, S. Rentenberger, G. Langer, J. Keplinger, W. Kern, and E. Zojer, *Adv. Funct. Mater.*, **15**, 403 (2005).
(30) X. Gong, S. Wang, D. Moses, G. C. Bazan, and A. J. Heeger, *Adv. Mater.*, **17**, 2053 (2005).
(31) H. S. Hwang, A. A. Zakhidov, J.-K. Lee, X. André, J. A. DeFranco, H. H. Fong, A. B. Holmes, G. G. Malliaras, and C. K. Ober, *J. Mater. Chem.*, **18**, 3087 (2008).
(32) P. Blowers, D. M. Moline, K. F. Tetrault, R. R. Wheeler, and S. L. Tuchawena, *Environ. Sci. Technol.*, **42**, 1301 (2008).
(33) A. A. Zakhidov, J.-K. Lee, H. H. Fong, J. A. DeFranco, M. Chatzichristidi, P. G. Taylor, C. K. Ober, and G. G. Malliaras, *Adv. Mater.*, **20**, 3481 (2008).
(34) P. G. Taylor, J. K. Lee, A. A. Zakhidov, M. Chatzichristidi, H. H. Fong, J. A. DeFranco, G. G. Malliaras, and C. K. Ober, *Adv. Mater.*, **21**, 2314 (2009).
(35) J. K. Lee, M. Chatzichristidi, A. A. Zakhidov, H. S. Hwang, E. L. Schwartz, J. Sha, P. G. Taylor, H. H. Fong, J. A. DeFranco, E. Murotani, W. W. H. Wong, G. G. Malliaras, and C. K. Ober, *J. Mater. Chem.*, **19**, 2986 (2009).
(36) J.-K. Lee, M. Chatzichristidi, A. A. Zakhidov, P. G. Taylor, J.

A. DeFranco, H. S. Hwang, H. H. Fong, A. B. Holmes, G. G. Malliaras, and C. K. Ober, *JACS*, **130**, 11564 (2008).

(37) J.-K. Lee, H. H. Fong, A. A. Zakhidov, G. E. McCluskey, P. G. Taylor, M. Santiago-Berrios, H. D. AbrunÞa, A. B. Holmes, G. G. Malliaras, and C. K. Ober, *Macromolecules*, **43**, 1195 (2010).

(38) H. H. Fong, J.-K. Lee, Y.-F. Lim, A. A. Zakhidov, W. W. H. Wong, A. B. Holmes, C. K. Ober, and G. G. Malliaras, *Adv. Mater.,* **23**, 735 (2011).

(39) A. A. Zakhidov, J.-K. Lee, J. A. DeFranco, H. H. Fong, P. G. Taylor, M. Chatzichristidi, C. K. Ober, and G. G. Malliaras, *Chem. Sci.*, **2**, 1178 (2011).

(40) J.-K. Lee, P. G. Taylor, A. A. Zakhidov, H. H. Fong, H. S. Hwang, M. Chatzichristididi, G. G. Malliaras, and C. K. Ober, *J. Photopolym. Sci. Technol.*, **22**, 565 (2009).

(41) J. Huang, R. Xia, Y. Kim, X. Wang, J. Dane, O. Hofmann, A. Mosley, A. J. de Mello, J. C. de Mello, and D. D. C. Bradley, *J. Mater. Chem.*, **17**, 1043 (2007).

(42) D.-S. Leem, P. H. Wöbkenberg, J. Huang, T. D. Anthopoulos, D. D. C. Bradley, and J. C. deMello, *Org. Electron.*, **11**, 1307 (2010).

(43) P. Liu, Y. Wu, H. Pan, B. S. Ong, and S. Zhu, *Macromolecules*, **43**, 6368 (2010).

(44) G. Klärner, J.-I. Lee, V. Y. Lee, E. Chan, J.-P. Chen, A. Nelson, D. Markiewicz, R. Siemens, J. C. Scott, and R. D. Miller, *Chem. Mater.*, **11**, 1800 (1999).

(45) C. D. Müller, A. Falcou, N. Reckefuss, M. Rojahn, V. Wiederhirn, P. Rudati, H. Frohne, O. Nuyken, H. Becker, and K. Meerholz, *Nature*, **421**, 829 (2003).

(46) A. Charas, H. Alves, J. M. G. Martinho, L. Alcácer, O. Fenwick, F. Cacialli, and J. Morgado, *Synth. Met.*, **158**, 643 (2008).

(47) R.-Q. Png, P.-J. Chia, J.-C. Tang, B. Liu, S. Sivaramakrishnan, M. Zhou, S.-H. Khong, H. S. O. Chan, J. H. Burroughes, L.-L. Chua, R. H. Friend, and P. K. H. Ho, *Nat. Mater.*, **9**, 152 (2010).